Further Researches Concerning
Atomic Weights

OF

Potassium, Silver, Chlorine, Bromine,
Nitrogen, and Sulphur

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THEODORE WILLIAM RICHARDS

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IN COLLABORATION WITH

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EDWARD MUELLER, AND GRINNELL JONES
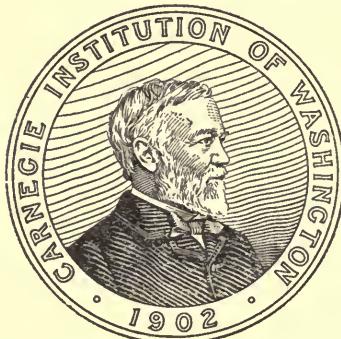
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By Theodore William Richards and Arthur Staehler

Contributions from the Chemical Laboratory of Harvard College

A Revision of the Atomic Weight of Potassium.

THE ANALYSIS OF POTASSIC CHLORIDE.

INTRODUCTION.

The atomic weight of potassium is a chemical constant of unusual interest and significance. Standing, as it does, in the middle of the series of five atomic weights of the most electro-positive metals — substances which exhibit in a highly marked degree both similarity and progressive change in properties — this number must be of unusual importance in the search for that undiscovered mathematical relationship which undoubtedly exists between these constants. Moreover, the atomic weight of potassium is essentially bound up with the atomic weights of oxygen, chlorine, and silver, this group forming a fundamental basis in the calculation of nearly all the other atomic weights; so that a change in the atomic weight of potassium has a widely ramified effect on the whole table of atomic weights. If any further evidence of this fact were needed, the recent paper of R. W. Gray[1] would furnish it.

The recent investigation upon the atomic weight of sodium by one of us in conjunction with Dr. R. C. Wells[2] showed conclusively that Stas's work, upon which rested earlier knowledge, was somewhat at fault in several respects. The most serious of these errors were, first, the existence of impurity in Stas's silver; secondly, the fact that in his work solid salt was dropped into the argentic solution, causing occlusion of salt; and thirdly, inadequate knowledge concerning solutions of argentic chloride. In view of these errors it seemed not impossible that a similar revision of potassium might likewise yield slightly lower results for potassium than had been found by this master of exact analysis. For this reason the present investigation was undertaken.

Before describing the present work a brief historical review of previous investigations may not be out of place. The determinations may be divided into two groups — the first group including all of these determinations in which the molecular weight of a potassic halide was found by decomposition of a chlorate, bromate, or iodate, and the second group, those in which data for determination of the relation of potassium to

[1] R. W. Gray, Journ. Chem. Soc. (Lond.), Trans., **89**, 1175 (1906).
[2] Richards and Wells, Carnegie Inst. of Washington Publication 28; Journ. Am. Chem. Soc., **27**, 459 (1905); Zeits. anorg. Chem., **47**, 56 (1905).

chlorine, bromine, or iodine were obtained.   The second group alone is concerned with the present work.

The early work of Berzelius, Pelouze, and Marignac need scarcely be considered here.[1]   It dealt for the most part with the precipitation of argentic chloride from a solution of potassic chloride and gave very widely discrepant results.   Even the later work of Marignac on chloride, bromide, and iodide of silver was of doubtful value, especially the last; and accordingly until the present research was undertaken, the atomic weight of potassium rested chiefly on the analyses of potassic chloride made by Stas, by Richards and Archibald, and by Archibald alone, and upon the analysis of potassic bromide made by Stas.

As in the case of sodium, Stas[2] made several series of determinations of the amount of silver needed to precipitate a known amount of potassic chloride.   One of these series was made in 1865, a later one in 1881, and yet another shortly before his death.   The earliest series, although in some respects more careful and thorough than the later ones, was greatly at fault, because in it he overlooked the solubility of argentic chloride. Accordingly of this work only the later need be considered.   The mean of seventeen analyses indicated that 100 parts of silver were equivalent to 69.122 parts of potassic chloride, corresponding to an atomic weight for potassium of 39.130, if silver is taken as 107.93 and chlorine as 35.473. Later, Richards and Archibald[3] found as a side issue of a research upon the atomic weight of cæsium that 100 parts of silver correspond to 69.115 parts of potassic chloride, and also that 100 parts of argentic chloride correspond to 52.022 parts of potassic chloride; and still more recently, Archibald[4] found results not very different.   With the values given above for silver and chlorine these results indicate a value for potassium of 39.123 and 39.128, respectively, in the case of Richards and Archibald, and 39.122 and 39.135, respectively, in Archibald's research.

In the case of the bromide Stas found in an unusually varying series of experiments that 100 parts of silver needed 110.346 parts of potassic bromide for complete precipitation, a result not very far from that of the less precise early work of Marignac.   If Baxter's value for bromine is accepted (79.953),[5] this corresponds to an atomic weight for potassium of 39.143, noticeably higher than the results from the chloride.   At that time the discrepancy did not appear, because the atomic weight of chlorine

[1]For a brief discussion of this work Clark's Recalculation of the Atomic Weights (1897) p. 41, may be consulted.
[2]Stas, Mém. Acad. Roy. Belg., **43** (1880) ; also Oeuvres Posthumes, edited by W. Spring.   See Clarke's Recalculation (1897), p. 42.
[3]Richards and Archibald (1903), Proc. Am. Acad., **38**, 443 (1903). Zeit. anorg. Chem., **34**, 353, 1903.
[4]Archibald, Trans. Roy. Soc. Canada [2], **10**, III, 47 (1904).
[5]Baxter, Journ. Am. Chem. Soc., **28**, 1322 (1906).

was not properly evaluated, Stas believing that his work on the chloride also indicated an atomic weight above 39.14.

In view of the fact that these results differ among one another to an extent beyond a reasonable limit of experimental error, it seemed advisable to investigate once more the atomic weight of potassium in order to detect the cause of the discrepancy. This appeared to be especially desirable on account of the recent gain in knowledge concerning the peculiarities of argentic chloride in solution. Accordingly, the present research was begun, and simultaneously another concerning potassic bromide. A description of the latter investigation follows immediately after this one.

An investigation upon atomic weights naturally resolves itself into several different portions — first, the preparation of the pure material; second, the method of drying and weighing this material; third, the details of the analysis and the calculation of the results. These will be considered in order in the following pages.[1]

PREPARATION OF THE MATERIAL.

POTASSIC CHLORIDE.

Several methods of preparing potassic chloride were tried, the most efficacious being adopted. The problem, of course, was to effect the elimination of other metals and other acids, especially those of the same groups. Both ends are most quickly and completely attained by incorporating into the process of preparation successive crystallization of different salts, in order to eliminate by the crystallization of one salt an isomorphous substance which might have been retained during the crystallization of another salt. The commonest salts of potassium were therefore studied in relation to their fitness for the elimination of impurities in this way.

In the first place, on account of the good results which Richards and Wells had attained in preparing pure sodic chloride from recrystallized sodic sulphate by precipitation with gaseous hydrochloric acid, sulphate of potassium also was early considered. This method was, however, soon abandoned, because the relative solubilities of potassic sulphate and chloride are far less favorable for the purpose than those of the sodium salts. The method of Archibald, who converted sulphate into chloride through precipitation with baric chloride, is complicated and involves the double work of preparing pure baric chloride as well as pure potassic sulphate. Moreover, it is not easy to eliminate the last trace of baric sulphate from the resulting salt. This also was rejected.

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[1] A somewhat less detailed statement of this work has appeared in the Berichte d. deutsch, ch. Gesel., **39**, 3611 (1906).

Next potassic chlorate was studied — a salt which had already been used by Stas for the preparation of pure potassium material. Both in crystalline form and in solubility this salt is very suitable for the separation of sodium from potassium material. Sodic chlorate crystallizes in regular crystals which are six times as soluble in hot water and sixteen times as soluble in cold water as the monoclinic crystals of potassic chlorate. On the other hand, the data concerning the crystalline form and solubility of the chlorates of rubidium and cæsium are not sufficient to enable one to make any certain prediction with regard to their behavior, and therefore experiments were made in order to discover whether or not these salts could easily be separated from potassic chlorate by recrystallization. The four salts of sodium, potassium, rubidium, and cæsium were mixed together and qualitatively separated by fractional crystallization. The sodium was effectively separated from the crystals; but after three careful crystallizations the cæsium line, although stronger in the mother liquor than at first, was still not absent from the crystals. Indeed, neither rubidium nor cæsium lines had considerably diminished therein. Accordingly, this method was also abandoned.

Potassic nitrate showed itself to be much more satisfactory in its behavior. Its usefulness did not seem at first so certain as to be a foregone conclusion, especially as Stas had not succeeded in preparing a particularly pure material from this salt. Probably this failure was due to the circumstance that he carried out the crystallization in glass vessels, which of course continually introduced sodium and silica. The rather inadequate data concerning the four nitrates may be well put together as follows:

	Solubility in 100 parts of water.				Crystalline form.
	Cold.		Warmer.		
	Temperature.	Parts.	Temperature.	Parts.	
	°		°		
$CsNO_3$............	3	12	60	Very many	Tetragonal.
$RbNO_3$..........	0	20	10	43	Needles.
KNO_3	14	25	114	337	Rhombohedral and rhombic.
$NaNO_3$..........	15	84	114	200	Rhombohedral.

Because this series of results is not entirely conclusive, although promising, a series of crystallizations was carried out here also. This series showed that an admixture of the three other nitrates with a large excess of potassic nitrate was nearly all eliminated by as few as two crystallizations. The separation of the sodium was especially marked

in the spectroscopic tests. This method, therefore, appeared very well suited for the preparation of pure potassium material, which might easily be converted into chloride after the other metals had been eliminated.

Pure potassic nitrate of commerce, obtained from Germany, was dissolved in a little water, freed from solid substances by filtration, and crystallized twice in Jena glass flasks. The salt was each time freed from the mother liquor in a porcelain centrifuge.[1] The resulting material was four times subsequently recrystallized in platinum vessels, and whirled in a platinum centrifuge. The pure crystals were now divided into two parts; one part was dried in a vacuum desiccator, while the other part was subjected to yet six more crystallizations and whirlings in platinum vessels.

It now became a question how this nitrate could best be converted into chloride. The method recommended by Stas of heating the salt with pure ammonium chloride involves not only the preparation of this latter salt in a pure state, but also great danger of contamination from the vessel, whether of platinum or porcelain. Platinum is especially attacked because of the action of the oxychlorides of nitrogen and of chlorine. The more favorable method appeared to be to convert the nitrate into chloride by repeated evaporation with hydrochloric acid in quartz dishes. This method was found to have two objections. In the first place, dishes large enough for the raw material were not to be had. Moreover, the tendency of the branching crystals to grow over the edge of the dish caused serious loss of material and danger of impurity. Neither could potassic nitrate be heated to a high temperature with ammonic chloride, or in the steam of hydrochloric acid in quartz dishes; for there is always danger that the reaction $4KNO_3 + 2SiO_2 = 2K_2SiO_3 + 4NO_2 + O_2$ would occur.[2]

Because Stas had never been able to obtain a salt free from silica when working in glass vessels, we desired to avoid completely the use of glass. Therefore, only one way remained, namely, to convert the potassic nitrate into chloride by precipitation with hydrochloric acid in a platinum dish. The resulting aqua regia must naturally attack the platinum, but we preferred this impurity to that of silica, and found, moreover, that the amount of platinum dissolved is very small. In the presence of large masses of potassic salts, aqua regia, especially in the cold, dissolves platinum but little. For example, in one experiment in which about half a kilogram of potassic nitrate was treated with hydrochloric acid gas, only three-tenths of a gram of platinum was converted into the form of potassic chlorplatinate. In subsequent crystallizations the amount was

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[1]Richards, Journ. Am. Chem. Soc., **27**, 105 (1905).
[2]Richards and Archibald, loc. cit.

very much less, because the great mass of the nitric acid was eliminated by the first crystallization. After the third recrystallization, the diphenylamin reaction failed to reveal the presence of any retained nitrate.

The precipitation was carried out in the following manner: The often recrystallized, very pure potassic nitrate was dissolved in the least possible quantity of cold water, contained in a platinum dish, packed in ice. Slowly, in order to prevent warming, hydrochloric acid gas was run into this solution. The gas was supplied by warming a pure concentrated solution, and was passed into the nitrate solution through an inverted platinum funnel. The potassic chloride, which appeared somewhat yellow from its slight platinic impurity, was whirled in the platinum centrifuge, and dissolved in purest water. Potassic chlorplatinate is practically insoluble in a concentrated solution of the chloride, as the law of concentration effect and the theory of ionization predicts; hence the impurity was easily separated upon a small, pure filter. The clear, colorless solution was again saturated with hydrochloric acid, and the same round of operations repeated. Upon a third repetition of this process, the nitric acid was eliminated and the salt, as a rule, was wholly colorless in consequence. On no occasion, even with large amounts of materials, did perceptible color remain after five treatments. No specimen was subjected to less than seven such recrystallizations, while some was passed yet five times more through the precipitation and centrifugal drying. Assuming that each time about three-quarters of the ordinarily adhering mother liquor was removed by the centrifugal separation, these crystals must have been as free from heteromorphous substances as if they had been recrystallized many thousand times in the ordinary fashion. It will be shown that all the samples gave the same results upon analysis, hence further purification according to this method was needless. The salt was found to be wholly free from sodium by a sensitive spectroscopic test. It was in every case freed from acid by a single recrystallization from the purest water, and by fusion in the manner to be described later.

Seven different samples were prepared after this fashion from varying raw material. These are given in the list below.

(a) The pure potassic material ("C. P." of German preparation) was recrystallized as nitrate six times, and precipitated as chloride seven times. This salt after the final recrystallization from pure water was dried in a platinum dish at 120° in an electric oven. The salt was snow-white, and was as clear as water when fused, as indeed, were all the other samples.

(b) This sample was similar to a, but obtained by the evaporation of the final aqueous mother liquor decanted from a. The mother liquor from b was rejected.

(c) Five extra precipitations with hydrochloric gas (or twelve in all) yielded this salt, which was prepared for analysis in the same way as a.

(d) This salt bore the same relation to c that b bore to a, being essentially identical with c.

(e) For this sample and the next one the nitrate was recrystallized twelve times, and the chloride precipitated seven times.

(f) From the final mother liquor of e, f was prepared, as b followed after a.

(z) This sample was exactly like a, except that the raw material came from an entirely different source.

ARGENTIC NITRATE.

The nitrate of silver used for precipitating chlorine in the analysis was crystallized three times from pure dilute nitric acid solution and each time centrifugally freed from mother liquor. Before each analysis the aqueous solution of the salt was tested in the nephelometer[1] for a possible trace of argentic chloride, and no material was ever used which showed to this exceedingly sensitive test the least trace of impurity. For preservation in a pure state it was kept in a tight desiccator over potash.

SILVER.

The metallic silver used in the research was made from argentic nitrate which had been six times recrystallized. The metal was precipitated as fine powder by ammonic formate,[2] melted on pure lime, and further purified by electrolysis.[3] The beautiful crystals thus prepared were fused in a stream of pure electrolytic hydrogen and finally in a vacuum of 0.1 mm. The metal was supported on a boat of the purest lime, prepared from calcic carbonate precipitated from the nitrate for this purpose. The boat was provided with several compartments, each of which held enough silver for one analysis, in order to avoid the possible introduction of impurity into the metal by subsequent cutting. It was inclosed in a stout porcelain tube, provided with Hempel water-cooled stoppers, and was heated electrically in a Heraeus tube-furnace.[4] The vacuum was maintained by a motor-driven Geryk oil air-pump. Except for these minor improvements, the preparation was essentially similar to the best methods employed by Richards and Wells in their often-cited work, to which the reader is referred for further details.

[1]Richards, Proc. Am. Acad., **30**, 385 (1894) ; Zeit. anorg. Chem., **8**, 269 (1895).
[2]Richards and Wells, Journ. Am. Chem. Soc., **27**, 475 (1905).
[3]J. L. Hoskyns Abrahall, Journ. Chem. Soc. Trans. (1892), 660; also Richards. Proc. Am. Acad., **28**, 22 (1893).
[4]Heraeus, Zeit. f. Elektrochemie, **8**, 201 (1902).

Very carefully tested preparations of commerce were used as the raw materials in the preparation of these acids. They were redistilled with platinum condensers until they were fully pure enough for the purposes for which they were needed. The hydrochloric acid had been shown in the research on sodium to be free from bromine or iodine.

WATER.

This substance, because it is used in larger quantities than any other, must be especially pure. All the water used, either for preparation or analysis, was twice distilled, once with alkaline permanganate and once alone. For the best work a platinum condenser was used. All that was needed for analysis was tested in the nephelometer immediately before use.

THE DRYING AND WEIGHING OF THE POTASSIC CHLORIDE.

The final preparation of the salt for analysis is given a special chapter to itself, because the proper execution of this feature is of very great importance, not less than the purification of the material. It is clearly useless to separate 0.001 per cent of a metallic impurity if 0.01 per cent of water is allowed to remain in the salt.

Obviously, superficial drying can not remove the imprisoned moisture in the crystals, hence they must be fused.[1] Except in a few preliminary experiments, where a common platinum crucible was used, this fusion was conducted in a platinum boat or open bottle contained in a porcelain tube through which a current of nitrogen was passing. The experience in a number of similar cases, that the simultaneous presence of oxygen and traces of hydrochloric acid inclosed in the crystals is likely to cause perceptible corrosion of the platinum boat, was confirmed in this case; hence an inert gas was needed. The nitrogen was prepared by the well-known method of Wanklyn, by passing air charged with ammonia over red-hot copper. The excess of ammonia was carefully eliminated by washing the gas with much dilute acid. Because fused sodic chloride was found to be essentially free from dissolved nitrogen, we did not think it necessary to fuse this very similar potassium salt in a vacuum.

Potassic chloride, although not so hygroscopic as some other salts, used in similar researches, is nevertheless far too hygroscopic to weigh safely when directly exposed to the air of the balance room. Its tendency to attract water was seen in perceptible crackling when the tube

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[1]Richards, Zeit. phys. Chem., **46**, 189 (1903).

containing fused salt was opened in the moist atmosphere of the beaker to be used for the solution of the salt.

At first the bottling apparatus so often used in the Chemical Laboratory of Harvard College was employed to protect the fused chloride from moisture during the determination of its weight, the chloride being contained in a platinum boat protected by a glass-stoppered weighing bottle. Because, however, the weighing room was not wholly constant in temperature or in moisture, time and trouble were needed to obtain exact weighings, even although the apparatus was always weighed by substitution against a similar empty boat and bottle. The use of quartz weighing bottles proved to be no advantage, indeed, if anything, a disadvantage. In either case, if time enough were taken, satisfactory weighings could be made; but as time was especially precious, another device was used which wholly overcame the trouble.

This effective and satisfactory device consisted in the use of small weighing bottles of platinum, shaped like the long Lawrence Smith crucible, which were closed by small platinum capsules, fitting into the bottles like ground stoppers. One of these bottles, containing the potassic chloride, was supported by a loop of platinum wire in an inclined porcelain tube, and above it in the tube was placed its platinum stopper. Glass stoppers fitted into each end of the porcelain tube, which was encircled by a suitable furnace. After the potassic chloride had been dried for a long time at a high temperature, just barely fused in nitrogen, and cooled in a current of pure dry air, the stopper was shaken into place and the platinum bottle quickly removed and placed in a desiccator. This arrangement is essentially similar to the bottling arrangement of Richards and Parker, except for the additional advantages that glass is wholly eliminated and that the inclosed air-volume in the tube is much smaller. Probably the burnished platinum joint is not as tight as the ground-glass joint; but it is amply tight enough to prevent any appreciable diffusion of moisture during the very brief exposure of the tube. This was evident from the constancy of the weighings, which were made by substitution against a similar empty platinum bottle kept in a similar desiccator. The weighings were very quickly performed and were trustworthy. Before being used, the platinum bottles were repeatedly ignited with pure sublimed ammonic chloride in order to remove iron; they remained satisfactorily constant in weight during subsequent experiments, the one used for the fusion losing only 0.3 mg. in fourteen experiments, or on the average 0.02 mg. in a single experiment. In one experiment, where oxygen was present during the fusion, as much as 0.3 mg. was taken from the boat, the platinum being plainly visible on solution. This was of course not used for analysis.

All weighings, whether of this salt or of silver or argentic chloride, were made by substitution in the manner already described in other papers.[1] The balance was a short-armed instrument made by Troemner, of the type adopted in other similar investigations; it was used only for this work and that to be described afterward. The weights were of platinized brass, carefully standardized according to the usual Harvard method.[2]

All weighings were reduced to the vacuum standard. Thus from every apparent gram of silver, 0.00003 gram was subtracted, and to every apparent gram of argentic chloride, 0.000071 was added, if the temperature was 20° and the pressure normal. Assuming the density of potassic chloride to be 1.995, the similar correction for this salt was $+ 0.000456$. Changes in temperature and pressure occasionally caused slight but usually inessential changes in these corrections.[3]

The wholly colorless, transparent, fused salt was dissolved in the purest water in a covered beaker of Jena glass under a tightly fitting bell-jar. The solution was always perfectly clear, except in the rejected case already cited and one other similar one. After this solution had been very thoroughly washed away and used for analysis, the platinum weighing bottle was heated for a short time in another crucible, and weighed in preparation for another analysis. The constancy of these weighings has already been discussed.

The details of preparation having been described, the analytical methods themselves must be indicated. The problem was, as in the case of sodium, to determine the amount of chlorine present, the weight of potassium being found by difference. Both of the previously used methods for finding the amount of chlorine were used, and the details are so much like those discussed by Richards and Wells[4] that much may be assumed as understood. For a full understanding of the present work, that upon sodium should be read in connection with it.

The two methods for the determination of chlorine, namely, the weighing of the precipitated argentic chloride on the one hand, and the discovery of the equivalent amount of silver on the other, are discussed below in order.

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[1]For example see Richards and Rogers, Zeit. anorg. Chem., **10**, 19 (1895); also Richards and Wells, Journ. Am. Chem. Soc., **27**, 465 (1905).
[2]Richards, Journ. Am. Chem. Soc., **22**, 144 (1900). These weights had an average density of 8.3.
[3]Richards and Wells, Journ. Am. Chem. Soc., **27**, 465 (1905).
[4]Loc. cit.

THE PRECIPITATION AND WEIGHING OF ARGENTIC CHLORIDE.

For purpose of analysis, the solution of potassic chloride was carefully and completely transferred to a large Jena glass Erlenmeyer flask with a finely ground glass stopper, and diluted to the volume of a liter or more. To this in the dark-room under the red light was added exactly the calculated weight of argentic nitrate, never more concentrated than one-fiftieth normal; and the mixture was shaken for a short time in order to aggregate the great mass of the precipitate. Because of the absence of an excess of argentic nitrate, the danger of the occlusion of this salt was slight. On the following day the supernatant liquid was usually quite clear, and to it now was added the excess of perhaps 0.05 gram of argentic nitrate needed for complete precipitation. This method of treatment was found to be more satisfactory than the immediate addition of all the argentic nitrate at once, as in this case long and tiresome shaking and washing of the precipitate was needed to eliminate wholly the occluded argentic nitrate. Thus was one of the chief difficulties met by previous experimenters almost entirely overcome. It was shown in the paper on sodium that the simplest test for the presence of argentic nitrate is the appearance of the argentic chloride after fusion, even a small trace of nitrate causing a perceptible gray-violet cloudiness. In all cases when the above precaution was used the fused mass was perfectly clear and transparent. This is, however, an anticipation of the later part of the process; the collection, ablution, and desiccation of the precipitate should first be described.

In preliminary experiments, the Gooch perforated platinum crucible with asbestos mat was used with all the precautions previously adopted in this laboratory. In this way it is certain that good results may be obtained; but the necessary second filtration of the filtrate in order to collect the traces of disintegrated asbestos is a tiresome process. On this account preliminary experiments were made with Gooch crucibles provided with a smooth and burnished mat of platinum sponge, as prepared by Heraeus.[1] Such crucibles are named by him after Neubauer, but might more properly be called Gooch-Munroe crucibles. In these tests it was found that such crucibles as a matter of fact answer very well for the purpose in hand if certain special precautions are taken. It is not permissible to ignite them at a high temperature, unless the precipitate also is to be ignited at a high temperature. A crucible brought to constant weight at 150° was found to lose 0.15 mg. on ignition, prob-

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[1]Zeit. Angew. Chem., **14**, 923 (1901). A number of experimenters have recommended and used a mat of platinum sponge in a Gooch crucible, but Munroe was probably the first. J. Analyt. Chem., **2**, 241 (1888). Also Chem. News., **58**, 101, 1885.

ably because of loss of previously adsorbed water. Moreover, when a dilute solution of argentic nitrate, potassic nitrate, and nitric acid, such as remains after an analysis, was passed through the filter, and this was five times washed with water, and dried at 150°, yet 0.15 more was gained, probably due to adsorbed salts. Very thorough washing after this brought the crucible back to its original weight after drying at 150°.

These experiments showed that the washing of the platinum sponge must be very thorough, and that a definite temperature must always be used for drying. Other experiments showed that constant weight could always be obtained, if these conditions were fulfilled.

It is well known that argentic chloride sometimes clings to a platinum surface, and always shrinks much on drying. On this account the somewhat delicate upper surface of the sponge was protected by a closely fitting disk or diaphragm of platinum punched with many fine holes. This diaphragm, merely laid upon the top of the sponge at the base of the crucible, was easily loosened with the precipitate, and formed an effectual protection for the sponge. After this was done, no platinum was ever lost from the upper surface; and none was ever carried away mechanically from below in the wash-water.

In spite of the presence of the disk, small particles of argentic chloride always clung here and there to the sponge. As a possible means of removing these when preparing for a new analysis, potassic cyanide was tested. It was found, however, that not only was this salt adsorbed by the sponge, but that in the presence of air platinum was dissolved even to the extent of a milligram — a fact not new, but none the less pertinent. Thiosulphate was not tried, because sulphur was an impurity little wished. Finally, while ammonia for a short time was inefficient, this liquid, when concentrated and applied for twelve hours or more, dissolved every trace of the silver salt without harming the crucible.

The technique of the Gooch-Munroe crucible having thus been mastered, this utensil was used with satisfaction as a means of collecting and weighing the precipitate in hand. The latter was first washed often by decantation, as is recounted below, and finally on the filtering crucible, which was dried to constant weight by a temperature gradually rising to 150°. After careful weighing, the main mass was separated from the clinging platinum disk, and was carefully fused in porcelain, as has often been described. The accurately determined loss on fusion, amounting sometimes to a milligram, was calculated from the part to the whole, and applied as a correction to the total weight of the precipitate.

This weight, even as thus corrected, did not, however, exactly represent the total in weight of the chlorine, as some of the argentic chloride was dissolved by the wash-water. The ablution had been conducted in three

stages, just as in the often-cited investigation of sodium. The first stage included the mother liquor and first five wash-waters, containing intentionally as much argentic nitrate as the mother liquor, and added to remove the greater part of the potassic nitrate. This first quantity of liquid was entirely free from chlorine in every accepted analysis, as was shown by careful testing in the nephelometer, and so was at once cast aside.

The second stage of washing was conducted with very dilute nitric acid, and yielded 0.5 or 0.6 liter of a very dilute solution of mixed nitric acid and argentic chloride and nitrate. The traces of chloride which it contained were carefully estimated in the nephelometer after addition of excess of argentic nitrate.

The third stage of the washing, also conducted with pure water acidified with nitric acid to prevent colloidal irregularities, yielded a liter or more of liquid containing much argentic chloride. The analysis of this liquid constituted a very important part of the work, and gave much trouble.

In order to be as certain as possible of the weight of chlorine it contained, this liquid was tested in five cases according to two very different methods. The first of these consisted in evaporation of the solution under diminished pressure and actual weighing of the precipitate, and the second consisted in a new modification of the nephelometer test. Although the latter evidently gave the more satisfactory results, the former is worthy of brief discussion, because its outcome certainly represents the maximum value.

In order to carry out these two parallel quantitative tests, the collected wash-water was divided into two parts; and the larger part, about 90 per cent of the whole, was evaporated under low pressure at 50° in a specially made Jena glass 2-liter flask with a glass stopper. In the course of this evaporation the argentic chloride began to separate out when the volume had been reduced to about 0.2 liter, if 2 mg. of the salt were present — a fact agreeing well with the recent observations concerning this solubility.[1] The dried residue was dissolved in a very little ammonia freshly distilled in platinum, and washed into a small precipitating flask, where it was reprecipitated with excess of argentic nitrate and nitric acid. This trace of precipitate was collected and weighed on a fresh Gooch-Munroe crucible in the same way as the larger mass. The results are given below in comparison with those obtained from the same solutions by the nephelometer.

An important modification was introduced into the nephelometric determination. One of us has repeatedly pointed out that in order to obtain satisfactory results with this instrument the solution to be tested and that used as the standard of comparison must be treated in exactly the

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[1]See for example Böttger, Zeitschr. phys. Chem., **56**, 93 (1906).

same way.[1]   Hence the use of a ground-glass plate[2] as a standard of comparison is a very questionable proceeding. It appears that the precipitation of argentic chloride from solutions of this salt differ perceptibly in mechanism from the precipitation of the same substance from other chloride solutions, even when argentic nitrate in great excess is used in each case.[3]   Accordingly, in order to secure a perfectly satisfactory comparison, both precipitates must be dissolved in ammonia and reprecipitated.   The precipitate then appears in each case in precisely the same condition, and yields trustworthy results.

The present tests were carried out in the following manner: Two test-tubes of precisely the same volume (0.025 liter) were provided.   Into one of these was placed 0.015 liter of the wash-water, and into the other, serving as the standard of comparison, a like volume of water containing about as much carefully measured chlorine (in the form of potassic chloride) as was present in the first.   Into each was now run 5 ml. of a three-hundredth normal solution of argentic nitrate.   The solutions were stirred with a platinum stirrer, previously cleansed with ammonia and the purest water.   After five minutes the precipitates were well formed; they were then both dissolved with the help of a milliliter of freshly distilled ammonia, and reprecipitated with a slight excess of nitric acid, being filled to similar marks near the top of the tubes.   The two cloudy solutions, thoroughly stirred, were allowed to stand and compared optically in the nephelometer in the usual way.

The following table compares the results obtained by the two methods. The varying solubility of the halide in the wash-water was mainly due to difference in temperature at the time of the ablution.

The Comparison of Weights of Argentic Chloride found Nephelometrically and by Evaporation.

Experiment No.	Volume.	Weights of argentic chloride.		
		By evaporation.	By nephelometer.	Difference.
	Liters.	*Mg.*	*Mg.*	*Mg.*
10	1.45	3.96	3.12	— 0.84
11	1.88	3.82	3.22	— 0.60
12	1.18	2.59	1.97	— 0.62
13	0.90	1.70	1.35	— 0.35
14	1.00	1.74	1.45	— 0.29

[1]Am. Chem. Journ., **31**, 242 (1904) ; **35**, 509 (1906).
[2]Wells, Am. Chem. Journ., **35**, 99 (1906).
[3]Richards and Wells, Carnegie Inst. Pub. **28** (1905) ; Journ. Am. Chem. Soc., **27**, 485 (1905).

Thus the nephelometer always indicated less argentic chloride than the gravimetric process.   At first the nephelometer was suspected, but the steadily diminishing difference between the two series of results indicated that they were approaching the point where they would indicate the same values.   As the nephelometric treatment was invariable, but on the other hand the evaporating-flask might easily be attacked, it seemed probable that the decreasing difference exhibited by the figures was due to something added to the weight of the precipitate from the latter source.   Apparently, as is reasonable, the flask was less and less attacked as it continued in use.

For this reason the gravimetric results were wholly rejected, and the nephelometric ones alone used in the calculation of the final results.

THE RATIO OF POTASSIC TO ARGENTIC CHLORIDE.

The final results of the series of analyses discussed above are recorded in the following table.   A number of preliminary experiments are omitted from this table, since it is clear that no doubtful or imperfectly executed experiment should find a place in such a table of final data. The list is nearly consecutive, however, as but few experiments met with misfortune after the processes had been mastered.   The original numbering of the experiments is retained; they were recorded in the notebook in chronological order.   All the argentic chloride referred to in this table was clear and colorless; a fact which is one of the best proofs that it was free from argentic nitrate or from organic dust.

Final Series of Determinations of the Ratio KCl: AgCl.

No. of Analysis.	Preparation of KCl.	Weight of fused KCl in vacuum.	Weight of fused AgCl in vacuum.	AgCl : KCl $= 100.000 : X.$	Atomic Weight K if Cl $= 35.473.$
		Grams.	*Grams.*		
13	*a*	4.36825	8.3986	52.012	39.114
14	*a*	5.56737	10.7038	52.013	39.115
15	*a*	6.41424	12.3323	52.012	39.114
20	*b*	3.27215	6.2913	52.011	39.112
31	*b*	4.83028	9.2870	52.011	39.112
Average......	....	....	....	52.0118	39.1134

This result will be discussed after the next series has been presented. It has a probable error, calculated by the method of least squares, of only about 0.0004; accordingly further repetition was deemed unnecessary.

THE RATIO OF POTASSIC CHLORIDE TO SILVER.

In this series of experiments, weights of the purest silver equivalent to entirely new portions of fused potassic chloride, as calculated from the preceding table, were dissolved in nitric acid, and the two equivalent solutions were mixed. Great care was used. The presence of an excess of silver or of chlorine was then determined with the nephelometer, exactly according to the details of manipulation adopted by Richards and Wells, whose accounts should be consulted for particulars. The table below contains the final results; the preliminary practice experiments are omitted for the same reason as before.

Final Series of Determinations of the Ratio Ag: KCl.

No. of Analysis.	Preparation of KCl.	Weight KCl in vacuum.	Weight Ag in vacuum.	Ratio Ag : KCl = 100.000 : X.	Atomic Weight of K if Cl = 35.473.
		Grams.	*Grams.*		
19	a	3.88074	5.61536	69.109	39.117
21	a	7.44388	10.77156	69.107	39.114
24	c	5.00681	7.24514	69.106	39.113
27	e	5.04833	7.30515	69.107	39.114
30	e	8.19225	11.85412	69.109	39.117
32	d	4.99795	7.23230	69.106	39.113
33	f	5.16262	7.47042	69.107	39.114
Average......	....	....	....	69.1073	39.1145

In this case the "probable" error is even somewhat less than before, being under 0.0004.

DISCUSSION OF FINAL RESULTS.

Thus two results have been obtained, giving for the atomic weight of potassium the value 39.113 by reference to argentic chloride, and the value 39.114 by reference to pure metallic silver. The close agreement of these results is an important evidence of their verity, and a striking confirmation of the new atomic weight of chlorine found by Richards and Wells. The atomic weight of chlorine is very simply calculated from the results of the two series above as follows: Cl = (69.1073/52.0118 − 1.00000) 107.93 = 35.475 — very near the most likely value, 35.473.

Such difference as exists is probably due to the slight remaining trace of occlusion of foreign salts by the argentic chloride. In the present case this source of error was eliminated more successfully than ever before, hence the agreement between the two values of the atomic weight of potassium was closer than usual.

It may be noted that the difference between the new value and the old value of Stas is somewhat less than in the case of sodium. Stas's results with potassic chloride led him to the value 39.146, about 0.032 higher than the new result, while with sodic chloride the difference was 0.042. A large part of this difference in each case is due to Stas's error in the atomic weight of chlorine; corrected for this error, the differences become 0.016 and 0.026, respectively. The differences are to be referred to the same causes in this case as in the others — namely, to Stas's incomplete knowledge concerning solutions of argentic chloride, to his practice of dropping solid salt into the precipitating solution, and to the presence in his preparations of traces of impurity taken from containing vessels. In the case of potassium one or more of these errors must have been less than in the case of sodium.

The results of Richards and Archibald, although very few in number and not intended to figure in a discussion of this kind, were somewhat better — probably because solid salt was never used directly in precipitation. Assuming the present research to yield the true value, their errors in the two series were, respectively, 0.009 and 0.014. The result of Archibald alone for the ratio of silver to potassium chloride was about the same amount (0.008) different from the present value; but his result for the other ratio was less satisfactory, having an error of 0.021, even greater than Stas's. These differences are not surprising, because less was known at that time than at present concerning the behavior of argentic chloride in solution.

Although the present paper presents strong evidence that the atomic weight of potassium is really as low as 39.114, more remains to be done. It would have been desirable to have used also some other wholly different method of preparing potassic chloride, and, moreover, to have evaporated large samples of the salt in nitrogen in order to discover a possible non-volatile residue. It is very doubtful if these additional experiments would have altered the present result, especially considering the precautions taken in the work and the result of the following research; but nevertheless it is planned to pursue these matters further.

Even when every conceivable precaution is taken, a single salt is not an adequate basis for the certain decision of an atomic weight. For this reason a parallel investigation on potassic bromide was simultaneously in progress at the Chemical Laboratory of Harvard College. The next communication, describing this other research, must be considered in connection with the work which has just been described. As will be seen, excellent confirmation of the present work is afforded by the work with the bromide.

SUMMARY.

This investigation concerning the quantitative composition of potassic chloride resembled in many respects the recent investigation of Richards and Wells on sodium.

In several details, however, improvements were introduced which effected a considerable saving of time and a perceptible gain in accuracy.

The precautions necessary for the accurate use of the Gooch-Munroe perforated crucible were ascertained; its employment was found to be advantageous.

Platinum weighing bottles with conical ground-platinum stoppers were used instead of boats and glass tubes for weighing the potassium salt.

Occlusion of argentic nitrate by the precipitated chloride was diminished by allowing the latter to stand for a long time in a solution containing neither excess of silver nor excess of soluble chloride, and by adding more argentic nitrate only after the precipitate had assumed a fairly permanent condition of aggregation.

The nephelometric estimation of small amounts of suspended argentic chloride was increased in accuracy by redissolving in ammonia both of the opalescent precipitates to be compared and reprecipitating, in order to equalize the conditions.

As final results, the outcome of twelve experiments, 100.000 parts of silver were found to correspond to 52.0118 parts of potassic chloride, and 100.000 parts of argentic chloride were found to correspond to 69.1073 of this salt.

The corresponding values for the atomic weight of potassium (if silver is assumed to be 107.930 and chlorine 35.473) are 39.1134 and 39.1145, in unusually close agreement.

II

A Revision of the Atomic Weight of Potassium

The Analysis of Potassic Bromide

By Theodore William Richards and Edward Mueller

A Revision of the Atomic Weight of Potassium.

THE ANALYSIS OF POTASSIC BROMIDE.

INTRODUCTION.

The foregoing quantitative study of potassic chloride by Dr. Arthur Staehler and one of the present authors affords strong evidence that the atomic weight of potassium is about 39.114, slightly lower than the value based upon the work of Stas. The authors fully appreciated, however, that the investigation of a single compound is not enough to establish a chemical constant so important as this, and, accordingly, the present investigation was prosecuted simultaneously. It was expected that the two investigations might either support one another or else, by affording incompatible results, lead to the discovery of a constant error in one or the other, and thus pave the way for further advance in knowledge. As will be seen, the work on the chloride was satisfactorily confirmed by the work on the bromide.

In the present case the careful study of potassic bromide was particularly necessary, because there already exist two concordant series of experiments upon this substance, performed by the old masters Marignac and Stas, pointing to a value in the neighborhood of 39.14, instead of the before-mentioned new value 39.11. In this case the higher value for potassium is not diminished, as in the case of the chloride, by an additive correction in the atomic weight of the halogen, because Baxter has ·shown Stas's estimate for bromine to have been nearly correct.[1] Hence the discrepancy remains one too serious to be tolerated.

The careful study of this work of Stas and Marignac affords convincing evidence that the potassic bromide used by them for analysis was not sufficiently pure for the purpose. Stas admitted that some of his preparations were not even wholly soluble in water, and his method of procedure was such that some of them probably contained platinum and hydroxide. Because speculations of this kind concerning work so long past are of but little value, it was clearly necessary to repeat this work with modern care; and the following pages recount the details of the repetition.

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[1] A brief review of Stas's and Marignac's work may be found in Clarke's "Recalculations" (1897), p. 47. Baxter's work is to be found in Proc. Am. Acad., **42**, 201, 1906; Journ. Am. Chem. Soc., **28**, 1322 (1906). See also Richards, Trans. Am. Phil. Soc., **43**, 116 (1904).

In common with others of the same type, the investigation easily resolves itself into several sections and will be discussed under the following heads : The preparation of materials; the drying and weighing of potassic bromide; the determination of the ratio of argentic to potassic bromide ; the determination of the ratio of silver to potassic bromide; and the discussion of the results. Of the laboratory tasks the preparation of the materials was by far the most laborious and puzzling, while the analytical work was comparatively simple.

THE PREPARATION OF MATERIALS.

THE SOURCE OF THE POTASSIUM.

The task of preparing pure potassic bromide, simple as it may appear, is by no means an easy one. In view of our experience, it seems probable that neither Marignac nor Stas ever prepared samples pure enough to correspond with the other precautions which they took. As in the case of sodic bromide,[1] the salt itself when once made can not be effectively purified. In this respect it differs widely from the chloride. We found after due trial that the potassium and bromine must be purified separately in such forms as to introduce no foreign matter. Accordingly, the two substances, already adequately purified, were caused afterwards to yield potassic bromide ; and this salt, when recrystallized, gave the final substance for analysis. The purification of the potassium materials will be discussed first.

It was necessary to provide potassium material which should be free from the suspicion of introducing any impurity with the metal desired, either basic or acid. Potassic nitrate, which had served so well in the case of the chloride, was not suitable for the present purpose, because the destruction of the nitric acid involves too great a sacrifice of laboriously prepared hydrobromic acid. After due consideration, potassic oxalate was tentatively chosen. It was necessary to prove that this salt can be easily and certainly purified by recrystallization, and especially to show that the other alkali metals can thus be separated. The following tests accomplished this proof.

A saturated solution of potassic oxalate containing a purposely added admixture of 10 per cent of sodic oxalate was crystallized and the crystals drained centrifugally. By the flame test, a pronounced difference was noticeable between the amount of sodium present in the mother liquor and that in the crystals. A second recrystallization and whirling was still more satisfactory ; the crystals gave no sodium test to the eye, while

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[1]Richards and Wells, Proc. Am. Acad., **41**, 435 (1906) ; Zeit. phys. Chem., **56**, 348 (1906).

the mother liquors gave a distinct yellow. This indicates that sodium has a decided tendency into the mother liquors, and hence can be separated by fractional crystallization.

Again, 1 per cent of lithium salt was added to potassic oxalate with similar outcome. Rubidium and cæsium were tested likewise. A saturated solution of potassic oxalate and a salt of each of these metals was made of such strength that the rubidium or cæsium could easily be found by means of the spectroscope. Each solution was evaporated until saturated, and cooled; and the crystals were whirled. The mother liquor gave a test for the impurity, the crystals gave none.

No other oxalates were seriously to be feared, because the insoluble ones would appear at once and demand filtration, and soluble double oxalates could hardly be isomorphous, and would therefore tend into the mother liquors. Traces of calcic oxalate in fact appeared in the former fashion, and traces of iron in the latter.

In view of these satisfactory results, it was evidently only necessary to crystallize the potassic oxalate often enough to make the separation complete; and since potassic oxalate has a fairly convenient change in solubility with the temperature, the yield after a considerable number of crystallizations is good, especially if pains are taken to carry out the process systematically.

Two very pure samples of oxalate were made, from two different sources. As one source of material, a commercial sample prepared by Merck was used. It had been labeled "Potassium oxalate, neutral, highest purity," and contained as a matter of fact only the traces of calcium and iron already referred to, but no lead or other discoverable impurity. A large quantity of a solution of this salt was filtered hot into a platinum dish, where it was five times systematically recrystallized, the crystals being centrifugally whirled each time.

Careful scrutiny in the spectroscope revealed in the product no other spectroscopic lines than those of potassium, and careful qualitative tests proved the absence of lead and iron. The salt dissolved without a trace of residue in water, and was quite pure enough to serve as a starting point for further operations, to be described under the heading "Potassic bromide."

A second sample of potassic material was obtained from Merck in the form of the hydroxide, being marked "Potassium Hydrate, Chemically Pure Reagent; Conforms to the standards of Dr. Krauch." It was in fact very pure, giving a perfectly clear solution both before and after neutralization. It was neutralized with a specimen of oxalic acid which had been carefully purified by Mr. G. E. Behr, jr., for other work. This acid contained no halogens, and left no residue on volatilization in plati-

num.   Slightly more than the equivalent quantity of acid was added, and
the oxalate obtained was therefore slightly acid.   As will be shown, the
acidity was later the cause of much inconvenience, and had better have
been avoided.   The oxalate was four times systematically recrystallized in
platinum with centrifugal draining each time.   The final product, like the
previous one, gave no tests for impurities except a slight excess of acid;
it was used as the source of potassium for one preparation of potassium
bromide.

<div align="center">BROMINE.</div>

Although the methods previously used at Harvard had afforded a
satisfactory yield of very pure bromine,[1] it was desired to add to the
knowledge on the subject by testing another method.   Through the gener-
osity of the Mallinckrodt Chemical Works of St. Louis, Missouri, and
also of the Dow Chemical Works of Midland, Michigan, a large quantity
of potassic bromate was placed at our disposal.   Repeated crystallization,
very kindly carried out for us on a large scale by these firms, had been
the method used in its purification.

This material, which served as our starting-point, was already very
pure, a fact which was indicated by three syntheses of argentic bromide
from purest silver and potassic bromide obtained by decomposing the
Mallinckrodt bromate.   These syntheses, carried out with all necessary
precautions, gave, respectively, 57.441, 57.440, 57.441 as the percentage of
silver in argentic bromide.   According to Baxter the true amount is
57.445.[2]   The slight difference indicates a trace of iodine rather than
chlorine; but this impurity can be easily expelled, while chlorine is far
more troublesome.

It having been demonstrated that recrystallization is an effective means
of purifying the salt from chlorate and chloride, a large quantity of
potassic bromate was three times recrystallized in porcelain, the crystals
being centrifugally whirled each time and all mother liquors discarded.
This gave an exceedingly pure bromate, much purer than Stas could have
obtained,[3] because the centrifugal draining makes so great a difference
in the rate of purification.[4]

A large quantity of the salt was decomposed into the bromide in a
platinum dish by the heat of an alcohol lamp.   The potassic bromate in
decomposing attacked the platinum, and the mass of bromide was slightly

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[1]See Proc. Am. Phil. Soc., **43**, 119 (1904), for references and Stas, Mém. Acad.
Belgique, **43**, II, 38 (1882).
[2]Baxter, Journ. Am. Chem. Soc., **28**, 1332 (1906). See also Richards, Trans.
Am. Phil. Soc., **43**, 119 (1904).
[3]Untersuchungen, 160.
[4]Richards, Journ. Am. Chem. Soc., **27**, 104 (1905).

brownish in color, but this caused no inconvenience in the present case, as the bromine was to be subsequently distilled. In order to liberate the halogen, the bromide was treated in strong solution with less than the calculated quantity of bromate and an excess of pure sulphuric acid. The acid was added drop by drop to the mixed solution of salts in an apparatus made entirely of Jena glass, which was kept surrounded by ice-water. The bromine which volatilized on account of the heat of the reaction was caught in a condenser under water; to this was added the remaining bromine, which had been separated from the supernatant solution by means of a separating funnel.

The bromine thus obtained was twice distilled by steam heat into water in a Jena glass condenser, packed in ice. It was kept in a well-seasoned bottle with double ground-glass stoppers.

The product was certainly free from non-volatile materials, and could have contained only iodine and perhaps a trace of sulphuric acid as impurity. It will be seen that these were eliminated in the subsequent work. This was the only sample of bromine prepared; it was used in all the preparations of bromide, as the quantitative results indicated that it was very pure.

POTASSIC BROMIDE.

The problem of obtaining potassic bromide from the oxalate and bromine had been carefully considered before these substances had been prepared. Only two methods recommended themselves for the present purpose, although the bromide can be obtained from these two materials by a variety of reactions, which would ordinarily be acceptable. Here, however, simplicity, completeness, and theoretical correctness must all be fulfilled; that the methods adopted really possessed these advantages in their favor must be admitted after careful perusal of the following description of the details.

In some preliminary experiments it was shown that by adding an excess of bromine to the oxalate and evaporating off the excess, a very pure bromide quite free from oxalate is obtained. Accordingly, a quantity of the first sample of five times crystallized potassic oxalate was treated with an excess of bromine, the bromine being added in small quantities from a dropping-funnel. The solution was held in a quartz dish, which was carefully hooded to prevent entrance of dust. When the action had ceased, the solution was heated on a steam-bath until any traces of iodine and all excess of bromine had been expelled. The solution was found to be entirely free from oxalic acid upon testing with calcic nitrate in a solution faintly acid with nitric acid. Although it was wholly colorless while in the quartz dish, after being concentrated in platinum it developed a very faint yellow tinge. Upon recrystallizing three times this color was

finally concentrated in the extreme mother liquor, and was found to be due to a trace of platinum; no iron was present. Even the first crystals were perfectly white, the second and third mother liquors also showed no trace of color, and only the first of the mother liquors gave a test for platinum.

The material thus prepared, after being three times recrystallized in platinum with centrifugal draining, was called sample I, and served for analyses 1 to 11.

The second sample of potassic bromide was prepared from the second sample of four times recrystallized potassic oxalate. The method was the same as with the previous sample. An excess of bromine was added to the oxalate in quartz; when action ceased, the bromine was driven off by heating on a steam-bath. However, on testing for oxalate, a perceptible quantity was found still undecomposed. This was unexpected, in view of the fact that the first preparation of bromide had given no trouble in this respect. The difficulty was traced to the presence of a small percentage of acid salt in the oxalate; the presence of acid has an inhibitory effect on the reaction of bromine on the oxalate ion. Obviously, the simplest remedy would have been to add pure potassic hydroxide; but this was not added because at that moment there was none at hand. Moreover, because the reaction was being performed in quartz, it was thought best not to use a caustic alkali for fear that the dish might be slightly attacked. The addition of a small amount of very pure recrystallized bromate to this slightly acid solution served better, because its use was unattended with danger. Its employment was entirely effective; the ionized hydrogen was removed, and after adding more bromine and heating, a solution of bromide was obtained which contained no trace of oxalate.

This specimen was recrystallized entirely in quartz, in order to prevent a recurrence of the trouble experienced with sample I, as well as to see if the variation of conditions affected the atomic weight. Two crystallizations were made with centrifugal draining, and every precaution; and there was obtained finally a very pure, colorless product with which were made two analyses, Nos. 12 and 13. That a uniformly pure material had been made is shown by the close agreement of these two analyses with the mean of all.

As a further precaution against accidental error, it was thought best to develop a method essentially different from that just discussed, and to prepare therewith a third specimen of bromide. In brief, this method consisted in the separate preparation of pure ammonic bromide and potassic hydroxide, and the production of potassic bromide by the evaporation of the mixed solutions of these substances. Thus can be obtained a salt contaminated only with excess of volatile ammonic bromide.

The preparation of pure ammonic bromide was very easy. Ammonia essentially free from carbon compounds was redistilled into water in a platinum dish. Into this was dropped the purest bromine, which fell through the liquid into a small porcelain crucible resting on the bottom of the dish. In this way the bromine itself could not come into contact with platinum and attack it. The reaction took place very rapidly, yielding ammonic bromide which could have contained no non-volatile ingredients, because all its constituents had just been distilled.

The preparation of pure potassic hydroxide was less easy to devise, because more original; but the execution was almost as easy. The problem was solved by the use of an electrolytic process which will be described in greater detail elsewhere. In brief, a saturated solution of potassic oxalate (sample I) was electrolyzed between a pure mercury cathode and a platinum anode in a porcelain dish cooled with ice, the current from four storage cells being used. When the amalgam became solid, the current was stopped, the solution decanted, and the amalgam washed, being triturated with an agate pestle under water, till no test for oxalate could be obtained. The pure amalgam was transferred to a platinum dish, covered with water, and made the anode of a dense current until only a little of the potassium amalgam remained undecomposed. Thus pure potassic hydroxide was formed. This solution was poured into the ammonic bromide solution, the mixture was evaporated and crystallized, and the salt thus obtained used for analyses 14, 15, and 16.

The bromide thus obtained must have been very pure. During the electrolysis, the high concentration of the potassic oxalate[1] would tend to allow the deposition of potassium only.[2] At any rate, metals less easy to deionize could hardly have been set free. During the later decomposition of water by the amalgam, all metals with less tendency to ionize would have remained in the mercury, because some of the amalgam was left undecomposed. Any trace of iodine which the bromine may have contained must have been driven off by the fusion just before analysis, this fusion being prolonged in order to expel ammonic bromide. The results of the analyses of this sample indicate its essential identity with the two preceding preparations. Since there was no known source of impurity in any one of the preparations, this was not surprising.

Although our consistent employment of insoluble vessels rendered the presence of colloidal silica unlikely, an effort was made to test for this impurity of sample II by volatilizing 3 grams of it in a stream of nitrogen. Unfortunately, the high temperature of the electric furnace caused the platinum boat containing the salt to weld to the foil which

[1]See Bunge, Berichte, **9**, 78 (1876).
[2]Berthelot, Ann. Chim. Phys. [5], **18**, 433 (1879).

surrounded it in the tube, so that no certain quantitative evidence could be obtained.   Two minute black spots were visible in the boat; nothing else could be seen upon very careful scrutiny.   If there were any silica present, the amount must have been too small to have had any appreciable influence on the final atomic weights.   Time and material were lacking, hence the experiment was not repeated.

SILVER.

The essential details of the preparation of pure silver, as developed by Richards and Wells, were followed in detail, and the reader is referred to their paper, as well as to the preceding paper of Richards and Staehler, for the particulars.   Two samples of silver were made; they were found to be identical in quantitative behavior.

The source of the material used for the first preparation was the pure precipitated argentic chloride remaining from the work of Richards and Wells on sodium.   It was reduced to metallic silver with invert sugar in a strong solution of sodic hydroxide.   The silver thus obtained was washed free from soluble matter and dissolved in nitric acid; the argentic nitrate after crystallization and whirling was reduced with ammonic formate, yielding a beautiful crystalline mass of metal.

This pure silver, after very thorough washing, was fused on lime by means of a blast lamp whose tip had been carefully cleaned.   The buttons which were thus obtained were cooled in the reducing-flame, washed free from lime, scrubbed with cleaned sea-sand, etched with strong nitric acid, and washed with the purest water, to serve as anodes in the electrolytic purification which was the next step.   The electrolysis was carried on as already described in previous similar Harvard researches, and every step of the subsequent work may be found in detail in the preceding papers on sodic and potassic chloride.[1]   The metal was finally fused as usual on a boat of the purest lime in an atmosphere of hydrogen under a tension of 50 mm.   The larger pieces, after etching with nitric acid, were cut into smaller ones of convenient size with a clean cold-chisel.   They were again etched in order to dissolve all traces of iron,[2] scrubbed with clean sand, washed with a jet of water, and etched yet again with acid, paying particular attention to the cut edges.   Finally the pieces were dried over an alcohol lamp and kept in a desiccator over potassic hydroxide for use.

This silver was used both in most of the titrations against potassic bromide and as the source of argentic nitrate used in the precipitation of argentic bromide to be weighed.

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[1]See Proc. Am. Acad., **38**, 450 (1903) ; and Richards and Wells, Journ. Am. Chem. Soc., **27**, 473 (1905) ; Richards and Staehler, preceding paper.
[2]Richards and Archibald, Proc. Amer. Acad., **38**, 450 (1903) ; Baxter, Journ. Am. Chem. Soc., **28**, 1329 (1906).

A second sample of silver, prepared from somewhat less pure initial material, was put through a more elaborate and exhaustive round of purification which need not be detailed. The preparation included five crystallizations as nitrate and two successive precipitations as metal by formate. This silver was fused into buttons of a size suitable for immediate use without cutting. They were cleaned by etching and washing, dried and preserved free from impurity as usual, and were used in analyses 7 and 9.

NITRIC ACID.

For preliminary work, ordinary "chemically pure" nitric acid was distilled once, using a platinum condenser and Jena glass receiver, the first third of the acid being discarded. For the final analyses this redistilled product, already very pure, was once again distilled, as before, the first third being rejected. This distillate gave no test with the nephelometer, after dilution.

WATER.

As usual in such work, all the water used had been carefully purified by double distillation, once from a fairly strong solution of alkaline potassic permanganate, and then alone. The distillate was caught in Jena glass receiving flasks which were provided with special adapters to prevent the access of dust. The first and last fractions were always rejected, only the middle portion being used. The connection of the Jena glass boiling-flask with the pure tin condenser was made without rubber or cork.[1] Such water gave every evidence of sufficient purity, as has been frequently pointed out.

THE LABORATORY.

A very essential precaution in every stage of this work was to effectually exclude hydrochloric acid. Accordingly, all the preparations of the bromide were carried out in a private laboratory, used especially and only for this work, and wholly free from the interference caused by large classes or other researches. Great care was taken not to allow any hydrochloric acid in the room; indeed, not a drop was used there during the entire research. A separate ventilating fan prevented fumes from other laboratories from interfering with the work.

UTENSILS.

As usual, great care was taken to avoid the use of any vessels which under the given conditions might be attacked and thus pollute the substance in hand. When glass and porcelain were not harmful, as in the early stages of the preparation of silver, such receptacles were employed; but in the purification of the substance for analysis, platinum and quartz were always used.

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[1] Richards, Proc. Am. Acad., **30**, 380 (1894).

THE DRYING AND WEIGHING OF POTASSIC BROMIDE.

For reasons already mentioned in the paper on potassic chloride, the salt under investigation must be fused before weighing. Unfortunately, potassic bromide when fused in air in a platinum vessel attacks the platinum to a considerable extent. Although it is shown later that this action does not seriously affect the weight of silver needed to precipitate the bromine in the salt, it was nevertheless desirable to avoid all such irregularities. No such action is observed when the fusion takes place in an atmosphere of pure dry nitrogen. Accordingly, in all work to be recounted, the potassic bromide was protected in this way during its fusion in a well-seasoned platinum boat, and was finally, by means of the Harvard "bottling apparatus," shut up in a tight weighing bottle in an atmosphere of pure dry air. The details have already been adequately given in several places, especially in the account of the recent work on the atomic weight of cæsium.[1] The only difference in the present procedure was demanded by the high fusing-point of potassic bromide (750°); on account of this, a porcelain ignition-tube was substituted for one of glass, as in the case of calcic chloride.[2]

Even with all possible care, however, the platinum boat was distinctly attacked, almost always losing in weight during the fusion. In two of the cases — analyses 1 and 14 — where the potassic bromide was fused for some time in the boat, the corrosive action was very considerable, causing losses of weight of 0.0007 and 0.0014 gram, respectively. One would be disposed to reject these determinations entirely, except for the fact that their average result, $\dfrac{\text{KBr}}{\text{Ag}} = 1.10317$, is almost exactly identical with that of the average of results 5 and 6, in which the boat was scarcely attacked at all, namely, $\dfrac{\text{KBr}}{\text{Ag}} = 1.10318$. Instead of being rejected, these results are therefore retained and used as evidence that even a considerable amount of dissolved platinum has no perceptible effect on the weight of silver precipitated by the salt. In a majority of the other cases, the change in weight of the boat during the fusion was less than 0.0001 gram. The average loss in analyses 10, 11, 12, and 16, in which the argentic bromide was weighed, was less than 0.00009 gram; hence even if platinum had been present in the potassic bromide in a state of fine division it could not have exerted any essential effect upon the result of this series of analyses.

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[1]Richards and Archibald, Proc. Amer. Acad., **38**, 451 (1903) ; Zeit. anorg. Chem., **34**, 362 (1903).
[2]Richards, Journ. Amer. Chem. Soc., **24**, 374 (1902).

As a matter of fact, the potassic bromide always gave a perfectly clear aqueous solution except once, namely, in analysis 14. In this case several small flakes of platinum were noticed in the salt both before and after the salt was dissolved in water.

The solutions were always perfectly neutral to phenolphthaleïn, a fact which is adequate proof of the retention of all the bromine during fusion, and also of the absence of oxalate from the potassic bromide crystals.

The third sample of potassic bromide had contained ammonic bromide, which was expelled during the fusion. During the expulsion of this salt, the boat was placed near the exit end of the porcelain tube, and there gradually heated to redness in a current of nitrogen. During the entire operation the middle portion of the porcelain tube was kept red-hot in order to prevent backward diffusion of the ammonic bromide, which by condensing might later cause a contamination of the potassic bromide. All the ammonic bromide having been sublimed, the boat was pushed into the middle of the tube, and the potassic bromide fused as described above. There being a possibility that even at the fusing-point of potassic bromide some ammonic bromide might still be retained, another portion of the same third sample of bromide was fused under approximately the same conditions as in the analyses. The solution of the bromide thus obtained was submitted to the Nessler test, being compared with a tube of pure water containing the same amount of reagent. No color was visible in either tube, hence no appreciable amount of ammonic bromide remained to contaminate the potassium salt.

The salt thus prepared for analysis was weighed in its glass-stoppered weighing-bottle by substitution, using as the substituting tare a precisely similar weighing-bottle. Successive weighings of the same specimen were always practically identical. The balance and weights were similar to those used with sodic and potassic chlorides, and all the precautions were the same. At each weighing the heights of the barometer, the temperature of the balance-room, and the humidity as indicated by a hygrometer were recorded. The density of the displaced air could thus be determined for each case. The variations from the average were, however, not enough to affect essentially any of the results, as weighings were not made under any abnormal atmospheric conditions. The weights were of course standardized by the usual Harvard method.

The specific gravity of potassic bromide must be known to within five one-hundredths of a unit in order to correct the weighings to the vacuum standard with sufficient accuracy. Its determination[1] has been undertaken with a variety of methods, with a variety of results, ranging from 2.20 to

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[1]For the literature see Landolt u. Börnstein (Meyerhoffer). Physikalisch-Chemische Tabellen (1905), and Clarke, Constants of Nature (part 1), Macmillan (1888).

2.756. The more recent results all tend towards the highest value, found by Krichmeyer[1] (2.756). This appeared to be the most probable, because the usual errors cause low results; but as this determination was made with only a single crystal, and as the salt weighed in the present research had been fused, it was thought best to investigate further. Accordingly, a pure sample of potassic bromide was further purified by being three times recrystallized with centrifugal draining, when it gave no flame test for sodium.[2] This product was fused in platinum and coarsely pulverized; its specific gravity was determined in an Ostwald pycnometer, modified for use with solids, using toluol as the fluid to be displaced. The toluol had been redistilled and possessed a density 0.8608 at 25°, referred to water at 4°; 8.2568 grams of potassic bromide displaced 2.6009 grams of the toluol at 25°, a result which indicates a density of 2.73. Time was lacking for a repetition of the experiment, but this preliminary result was enough to show that the fused salt is essentially in the same state as the crystallized salt. The difference between the two values is too small to affect the vacuum correction; the average value 2.74 was used.

THE PRECIPITATION AND WEIGHING OF ARGENTIC BROMIDE.

In order to determine the weight of argentic bromide obtainable from the bromine in potassic bromide, the latter salt was precipitated by a very slight excess of argentic nitrate, both substances being dissolved in large quantities of the purest water. The method differed but slightly from that which had been used recently in so many other cases of the same kind. The argentic nitrate was prepared from a weighed amount of pure silver, but no attempt was made in this series to determine the exact amount of silver required, as it was desired not to complicate the process before weighing the argentic bromide. Care was taken to have an excess, but only a slight excess. The silver was dissolved in nitric acid with all the usual precautions, and the precipitation was carried out in orange-red light in the dark-room devoted to accurate work of this kind. The potassic bromide had been dissolved out of the boat by digestion in a large platinum dish, and been transferred to a 2-liter glass-stoppered Jena Erlenmeyer flask with careful rinsing, and every precaution to prevent any gain or loss. After being well shaken, the flask containing the silver bromide was allowed to stand until the mother liquor had become clear. The solution was filtered through a platinum Gooch-Munroe crucible, and the precipitate was washed by decantation, first with an extremely dilute acid solution of silver nitrate, and finally with exceedingly dilute

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[1]Krichmeyer, Z. physikal. Chem., **21**, 81 (1896).
[2]See Krichmeyer's experience, loc. cit.

nitric acid to prevent colloidal solution.   With this latter faintly acid liquid the precipitate was transferred to the crucible.   The silver bromide was dried at least twelve hours in the filtering crucible at 130° in an electric oven,[1] and weighed.   It was then fused in a porcelain crucible, in a furnace where it was effectively protected from flame gases, in order to determine the trace of moisture always retained.   The wash-waters and the solution obtained on neutralizing the ammoniacal rinsings of the flask gave no indication of the presence of bromine on careful testing in the nephelometer.

In using the Gooch-Munroe crucible, all the precautions pointed out in the preceding paper were carefully heeded.   A perforated plate was always placed on top of the friable sponge to prevent rupture.   After each determination any bromide clinging to it was leached out with potassic cyanide, which was then washed away with nitric acid, and finally very thoroughly with water.   The solvent action of the cyanide occasionally loosened portions of the spongy film, but there was no difficulty in repairing the injury.   Upon drying in the electric oven, the crucible was ready for another analysis.

In addition to the loss of weight on fusion, two other very small and somewhat uncertain corrections were applied to the weight of the argentic bromide, but because they were of about the same magnitude and of opposite sign, their effect was practically negligible.   These were a correction for platinum corroded from the boat during the fusion of potassic bromide, and a correction for argentic bromide dissolved in the water used for washing.   Because these corrections have not been considered in most work of this kind, a word about them may not be amiss.

In the series under discussion the average loss of the boat in each determination was less than 0.00009 gram.   All of this trace of platinum may have been present as invisible dust in the solution, and thus may have been weighed with the argentic bromide, or all of it may have been in a soluble form and may have remained in solution.   Because of this uncertainty, a compromise was made, and half of the loss of weight of the boat (in the mean 0.00004 gram) was subtracted from each weight of argentic bromide.   As the average total weight of argentic bromide was over 4 grams, this compromise could not have introduced an error as great as 1 part in 100,000 in either direction.

According to Stas,[2] argentic bromide is wholly insoluble in water, but recent experiments show that in the flocculent form it is unquestionably soluble to a slight extent.[3]   As in the case of the chloride, its solubility is

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[1]Richards, Am. Chem. Journ., **22**, 45 (1899).
[2]Stas, Oeuvres, I, 89.
[3]Böttger, Z. für physik. Chemie, **46**, 602 (1903); Kohlrausch und Rose, Zeit. phys. Chem., 12, 234 (1893); also, Richards, Proc. Am. Acad., **30**, 385 (1894).

greatly diminished by the addition of an excess of either precipitant; but whether or not any is dissolved by a very dilute acid solution of argentic nitrate, such as that used in washing, it is practically impossible to discover. It is not unlikely, however, that about as much was dissolved by this solution as by the dilute hydrobromic acid used by Baxter in his admirable work on the atomic weight of bromine;[1] and in this solution it is easy to find the amount of dissolved substance. Baxter found as a matter of fact in his last seven most exact syntheses an average of 0.00004 gram of argentic bromide in each of the wash-waters — a figure which was added to each of our weights of argentic bromide, because the other circumstances of the analysis were similar in the two cases. On the average, this correction exactly eliminates the other; and except for the sake of completeness, they might both have been wholly neglected.

Of course all the weighings were corrected to the vacuum standard, by adding 0.000041 gram to every apparent gram of argentic bromide and 0.00029 gram to every apparent gram of potassic bromide, as calculated from the figures 6.473, 2.74, and 8.30, for the densities of argentic bromide,[2] potassic bromide, and the brass weights respectively. All the determinations made are given in the table below.

The Ratio of Argentic Bromide to Potassic Bromide.

Experiment number.	Weight of KBr in vacuum.	Corrected Weight of AgBr in vacuum.	Parts of KBr for 100.00 parts of AgBr.	Atomic Weight of Potassium Br = 79.953.
	Grams.	*Grams.*		
10	2.19027	3.45617	63.3728	39.114
11	4.19705	6.62285	63.3723	39.113
12	2.06723	3.26206	63.3719	39.112
16	2.58494	4.07889	63.3736	39.115
Total average...	11.0395	17.41997	63.3727	39.1135
Probable error..	....	....	0.0003	0.0004

The extreme deviation from the mean corresponds to an error of weighing the potassic bromide of 0.00004 gram, a reasonable quantity. The "probable error" indicates that there is but little chance that the atomic weight of potassium is much below 39.113 or much above 39.114, if constant chemical errors were successfully excluded. Stas found in a single experiment the number 63.383 instead of 63.373.[3]

With unlimited time more determinations might well have been made, but the agreement of these four results is so good that further repetition seemed to be not very urgent.

[1]Baxter, Journ. Amer. Chem. Soc., **28**, 1322 (1906).
[2]Baxter and Hines, Amer. Chem. Journ., **31**, 220 (1904).
[3]Stas, Untersuchungen (Trans. Aronstein 1867), page 340.

THE DETERMINATION OF THE SILVER NEEDED FOR PRECIPITATION.

The silver titration method of Gay-Lussac, as developed by Pelouze, Mulder, Stas, and more especially by the recent work at Harvard, yields very consistent and accurate results, if the proper conditions are carefully observed.   The reading of the end-point is rendered easy by the use of the nephelometer.[1]   In the case of the somewhat soluble chloride, various precautions must be strictly heeded; but with argentic bromide, which is almost insoluble, the matter is a simpler one, and a very slight excess of either bromide or silver can be easily determined.

The method used in the present case is easily inferred from previous Harvard work of the same kind.   From the weight of a piece of the purest silver, the equivalent amount of potassic bromide was calculated; slightly more than this amount of substance was then fused as before in a platinum-iridium boat placed in the porcelain tube of the bottling apparatus. From the weight of fused bromide, the equivalent quantity of silver was calculated; the greater part of the difference between this calculated weight and that of the original piece of silver was added in the shape of pure silver wire,[2] and any final difference of 0.1 or 0.2 mg. was made up with a dilute solution of silver nitrate.   The silver was dissolved in nitric acid and the nitrous acid expelled as usual, and the solution was then diluted to about tenth normal.

To the dilute bromide solution, with continual agitation, was added this dilute argentic solution; the total volume including the water used in rinsing usually amounted to about 1.5 liters.   After shaking steadily for 15 minutes, and occasionally for a day, the mixture was allowed to settle during another day.   When clear above, about 0.05 liter of the aqueous solution was withdrawn and tested in the nephelometer, one tube being treated with an excess of bromide, the other with an excess of argentic nitrate.   If any difference in the opalescence was noticeable after due time had been allowed for the very faint clouds to attain their maxima, the slight deficiency was made up in the flask by means of solutions containing approximately 1 milligram of argentic nitrate or of potassic bromide per milliliter.   These additions were continued till equality in the opalescence was attained.   From the sum of the original weights and subsequent additions, the total amounts of bromide and silver were obtained; from these, reduced to vacuum, the ratio was calculated.   All the analyses which were performed are given in the table, excepting No. 2, which was rejected for just cause before it was finished.   Vacuum corrections of $+$ 0.00029 for every gram of potassic bromide and $-$ 0.00003 for every apparent gram

[1]Richards and Wells, Am. Chem. Journ., **31**, 235 (1904).
[2]Richards and Parker, Proc. Am. Acad., **32**, 60, 1896.

of silver were applied. Most of these experiments were made before
those given in the preceding table, a fact which may account for the
slightly less satisfactory agreement of the individual results. Because the
deviations could not be traced to any definite cause of disturbance, they
must be ascribed to accident.

The Ratio of Potassic Bromide to Silver.

Experiment number.	Weight of KBr in vacuum.	Weight of Silver in vacuum.	Parts of KBr corresponding to 100.00 parts Ag.	Atomic Weight of Potassium if Br = 79.953.
	Grams.	*Grams.*		
1	4.33730	3.93164	110.318	39.113
3	4.18763	3.79587	110.320	39.115
4	4.15849	3.76943	110.321	39.116
5	3.67867	3.33450	110.321	39.116
6	3.60484	3.26776	110.315	39.110
7	4.78120	4.33387	110.322	39.118
8	5.67997	5.14860	110.321	39.116
9	6.41587	5.81571	110.320	39.115
13	2.88134	2.61184	110.318	39.113
14	3.64383	3.30309	110.316	39.111
15	3.12757	2.83504	110.318	39.113
Total average...			110.3190	[1]39.1143
Probable error..			0.0004	0.0004

[1] The average 39.1143 is calculated from the average 110.3190, not from the average of the individual values of
the atomic weights in the column above. The difference is of course very slight.

The "probable error" is as small as before because of the greater
number of determinations; and the mean deviation from the average value
is only one in the last decimal place. It will be observed that these results
point to the limits 39.113 and 39.115 as the extreme values between which
the atomic weight of potassium must fall, in essential agreement with the
previous results.

Marignac's seven experiments on this ratio give values ranging from
110.303 to 110.369, while Stas's fourteen results ranged from 110.332 to
110.361.

Obviously the results furnish a means of calculating the atomic weight
of bromine, when taken in connection with the foregoing series, entirely
independent of any other work. Thus Br = (110.319/63.3727 — 1.00000)
107.93 = 79.954, a value almost identical with Baxter's value, 79.953. This
is excellent proof that the bromine used in the present research was pure,
and that the occlusion of electrolytes by argentic bromide was small.

THE ATOMIC WEIGHT OF POTASSIUM.

The preceding paper and the present one together yield four ratios determined with modern precision, which together fix the atomic weight of potassium as definitely as could be expected. The respective values are as follows:

From the ratio of argentic to potassic chloride . . . . K = **39.1134**
From the ratio of metallic silver to potassic chloride . . . . K = **39.1145**
From the ratio of argentic to potassic bromide . . . . K = **39.1135**
From the ratio of metallic silver to potassic bromide . . . . K = **39.1143**

Average atomic weight of potassium, if Ag = 107.930 . . . K = **39.1139**

These figures are interesting and significant. The maximum departure from the mean is only 1 part in 70,000, and such differences as exist in the figures are explicable. It is likely that the slightly lower value given by the first member of each pair of series was due to a trace of occlusion of potassic nitrate by each of the precipitates — a circumstance which can not be absolutely prevented. Therefore the higher values, averaging 39.1144, are more probable. The differences are, however, wholly negligible at present.

In this connection it is interesting to note that Clarke in 1897, from a miscellaneous collection of partly uncertain results obtained by others, decided upon the almost identical value, 39.112,[1] although at the same time from similar results he obtained values much too low for chlorine and iodine, somewhat too low for bromine, and much too high for sodium.

The very close mutual agreement of the new results obtained from two different compounds is a satisfactory verification of the relative values yielded by the recent work on the atomic weights of chlorine and bromine.[2] The value of chlorine found from the work on potassium chloride was 35.475; and that of bromine from the present work is 79.954. The ratio of chlorine to bromine is thus found to be 0.44369, whereas the ratio computed from the work of Richards and Wells and of Baxter is 0.44367.

Against such an accumulation of concordant data as that just presented, the older figures can have no important weight. Whatever may have been the cause of the irregularity and internal inconsistency of Stas's results with potassic chloride and bromide, there seems to be little reason to doubt that the outcome of the present investigation, 39.114, really represents the atomic weight of potassium.

It is needless to point out that this change in the atomic weight of potassium will affect many other atomic weights.

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[1] Recalculations, p. 57.
[2] Richards and Wells, loc. cit.; Richards, Trans. Amer. Phil. Soc., **43**, 116 (1904); Baxter, loc. cit.

SUMMARY.

This investigation upon the atomic weight of potassium presents, among other considerations, the following additions to the knowledge of the subject:

(1) The problem of preparing pure potassic bromide was solved in two ways.

(2) An unusually satisfactory method for preparing pure potassium hydroxide was developed. This method is applicable to other alkalies, and will be described elsewhere in greater detail.

(3) The ratio of silver to potassic bromide was redetermined, and found to be 100.000 : 110.319. The atomic weight of potassium was thus found to be 39.1143, if silver is 107.930 and bromine 79.953.

(4) The ratio of argentic bromide to potassic bromide was found to be 100.000 : 63.373. This determination yielded an essentially equal value, $K = 39.1135$.

(5) These values confirm in a striking manner the simultaneously executed work upon potassic chloride, and unite with them in showing that the atomic weight of potassium is 39.114.

(6) By thus agreeing, these four values support the new value for the atomic weight of chlorine in relation to silver and bromine.

III

The Quantitative Synthesis of Argentic Nitrate and the Atomic Weights of Nitrogen and Silver

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By Theodore William Richards and George Shannon Forbes

THE QUANTITATIVE SYNTHESIS OF ARGENTIC NITRATE, AND THE ATOMIC WEIGHTS OF NITROGEN AND SILVER.

INTRODUCTION.

The composition of argentic nitrate is one of the questionable premises in the lively argument which has recently taken place concerning the atomic weights of nitrogen and silver.[1] Although Stas's syntheses of this salt were carried out on a large scale, and far more carefully than those of anyone before him, several points concerning the details of the work were not investigated with the care which modern physicochemical knowledge demands. Accordingly, a repetition of this work of Stas's seemed to be worth the trouble involved; and the following pages contain a brief account of nine months' thought and labor upon it.

The method appears at first sight to be extremely simple, consisting merely in the weighing of pure silver, the dissolving of this silver in nitric acid, and the weighing of the resulting nitrate. The preparation of pure silver having been already solved, the great difficulty consisted in the procuring of satisfactory evidence that the nitrate was free from impurity, and in making sure that none of the silver was lost during the process. The main emphasis of the subsequent discussion will therefore be laid on these points, the other details being often indicated with but few words, because they so closely resemble the details of previous investigations carried out in the Chemical Laboratory of Harvard College.

The research naturally divided itself into four sections, namely, first, the preparation of pure materials; second, the quantitative synthesis; third, the determination of the purity of the product; and fourth, the final result and its relations to the table of atomic weights. These will be considered in order.

PREPARATION OF PURE MATERIALS.

All the substances used in the research were purified with very great care. Nitric acid and silver were the two most important.

Nitric acid was supplied by two firms. Each sample was warranted by the manufacturers to be of a very high grade of purity. Each was redistilled twice just before adding to the silver, using only the middle

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[1]See especially Guye, Nouvelle Rech. s. l. Poids Atom. de l'azote, Soc. Ch., Paris, 1905. The reader is referred for a convenient résumé to the Report of the International Committee on Atomic Weights, Journ. Am. Chem. Soc., **28**, 1 (1906), and many other places; also to Clarke, Journ. Am. Chem. Soc., **28**, 293 (1906); Gray, Trans. Chem. Soc. (London), **89**, 1173, (1906).

portion of each distillate.   None of the samples left a trace of nonvolatile residue on evaporation.   No difference could be detected in the results because of the difference of source of the acid, nor was the constancy destroyed when a single distillation only was made.   (Experiment 11.) Hence little anxiety was felt concerning the purity of this material.

Silver. — The researches of Richards and Wells have shown how to prepare silver of unquestioned purity.   Preliminary determinations 1, 2, 3, 4, 5, 7, and 8 were made on a sample (A) left over from the above-mentioned research, crystallized fifteen times with nitric acid, precipitated with formate, and fused on purest charcoal, but not electrolyzed or fused in hydrogen.   No. 9 was made with a sample prepared by Professor Baxter for his final work on bromine.   It had been through the chloride and formate treatment, electrolyzed, fused in hydrogen, cut with a saw, etched with nitric acid, boiled with water, dried at dull redness in vacuo, and given us ready to weigh.   We are much indebted to him for furnishing this check on our silver.   The final determinations were made with silver derived from several preparations.   The first of these (C) was recrystallized sixteen times as nitrate from water and redistilled nitric acid, and then precipitated twice in succession with formate.   A part of the final formate product was fused on the best lime in carefully purified hydrogen made from aluminum and sodic hydroxide.   Sample D had been precipitated as chloride, reduced with best alkaline sugar, washed free from chloride, dissolved in nitric acid, filtered and crystallized as nitrate in platinum six times from nitric acid distilled in a platinum condenser. Centrifugal treatment eliminated the mother liquor.   The last crop of crystals was precipitated with formate in a silver dish, washed free from ammonia, and fused in a cup of pure lime.   Sample F was obtained by the electrolysis of a button of very pure silver from Colorado, which had been fifteen times recrystallized as nitrate, precipitated with formate, and fused on lime.   Samples C, D, and F were all cleaned by etching and then purified by electrolysis through a nitrate solution made from some of the same silver and the purest nitric acid.   They were then fused separately, on a well-seasoned lime boat, in a new porcelain tube, in an atmosphere of pure electrolytic hydrogen.   The Hempel stoppers fitted so well that the pressure could easily be reduced to a fraction of a millimeter by a Geryk oil-pump when desired.   The heating was accomplished by a large Heraeus electric furnace which fused the silver without overheating any part of the tube.   In all cases the initial fusion was completed in hydrogen at atmospheric pressure, but in half the fusions the tube was evacuated before the temperature was lowered.   No spurting or boiling could be observed through the glass window when the pressure was reduced, and

the silver thus prepared gave the same combining weight as that cooled under a full atmosphere's pressure of hydrogen. Thus the conclusion of Richards and Wells and of Baxter that silver can not dissolve a weighable amount of hydrogen was confirmed.

The buttons thus obtained were etched to remove lime, and if too large to go into the flasks used for the synthesis, were cut with a cold chisel or a jeweler's saw, observing all the precautions recommended by Richards and Wells. The fragments freed from superficial iron were washed and dried, sometimes in the electric oven in air at 150° for an hour, sometimes in a vacuum at dull redness, and sometimes in a reduced pressure of hydrogen. Judging from the constant combining weight, all these methods were equally good.

Water.— The water was distilled first with alkaline permanganate through a glass condenser, and then, after the addition of a small drop of dilute sulphuric acid, through a carefully cleaned condenser of block tin. Needless to say, dust was excluded as much as possible, and distillations were conducted immediately before the water was needed, in order to avoid absorption of gases or solution of solid matter.

Air.— It will be remembered that Stas allowed his solutions of argentic nitrate to evaporate very slowly, the vapors diffusing out through the neck of his flask and condensing in a suitable receptacle. Under these conditions the evaporation required seventy-two hours of continuous heating— an unnecessarily prolix process. To hasten the escape of aqueous vapor, it was resolved to maintain a gentle current of pure dry air throughout the process. The air for this purpose was delivered from a water pump, which must have removed some of the original impurities. It was passed first through a tall Emmerling tower filled with beads moistened with concentrated sulphuric acid, to which a trace of potassic bichromate had been added, and then through two more towers filled with a concentrated solution of pure potash, being thus freed from ammonia and from acid gases. Next it was passed through a tall drying tower of stick potash, to a hard glass tube containing platinized asbestos heated to dull redness by a Bunsen burner. The hot platinum was intended to destroy organic matter. Hence it passed into a trap designed to catch asbestos shreds, and finally, the air was dried by two towers of broken potash. The whole purifying train was put together without rubber, all the pieces being blown together except the hard glass tube, which was connected with the soft glass on either side with joints so well ground that no lubricant was necessary. The towers were glass-stoppered. Air thus purified and dried contains nothing to injure the silver nitrate except possibly a minute trace of ammonia, which might have come out of the potash solutions.

THE SYNTHESIS OF ARGENTIC NITRATE.

The materials having been prepared, the next step was to combine them. This combination must take place in a vessel wholly free from a suspicion of solubility on the one hand, and arranged so as to prevent loss of material on the other hand. At the same time, it was important to be able to evaporate and to weigh the argentic nitrate in the same vessel. After a careful consideration of the somewhat conflicting claims of these requirements it was decided to carry out the process in small round-bottomed flasks of fused quartz of from 0.03 to 0.04 liter capacity; with necks 11 cm. in length and 6 to 9 mm. in internal diameter. Collars of platinum wire provided with loops permitted the suspension of these flasks from the hook of the Troemner balance. Before weighing, they were heated in the oven to be presently described to 250° for at least half an hour, a moderate air-current sweeping through them all the time. The coverings were then lifted, and each flask was removed by a hook of platinum wire sealed into a glass rod, and transferred to a large desiccator provided with a suitable support. Two flasks similar in weight and surface were treated in the same way and kept in the same desiccator. After two hours near the balance the first flask was weighed against a tare, its weight being determined by substitution of the first by the second flask and a few small weights. Upon removal from the desiccator both flasks absorbed moisture from the air, often to the extent of 0.0001 gram, but they soon reached constancy with respect to one another, which was all that was needed. No final weighings were made when the hygrometer in the weighing-room stood above 40, and under these circumstances flasks could be weighed on successive days with variations not exceeding 0.00003 gram.

A new Troemner balance, sensitive to 0.01 mg. was available for the research. The brass weights were carefully standardized at the beginning of the year, and again upon starting the final series; and the rider also was calibrated, and the necessary correction employed. For correction to the vacuum standard 0.000132 was added to each apparent gram of argentic nitrate, and 0.000030 was subtracted from each apparent gram of silver. This was on the assumption that the two specific gravities concerned were respectively 4.35 and 10.49, that of the brass weights being 8.3.

The silver was now weighed by substitution, and carefully pushed down the neck of the flask, which was held meanwhile in a horizontal position to avoid breakage. Next the whole was transferred to a large, clean, empty desiccator, whose sides had been moistened; and the flask was laid on a suitable support of glass and platinum tilted 45° from the ver-

tical. A sufficient quantity of purest nitric acid mixed with half its volume of distilled water was poured in from the platinum crucible into which it had just been distilled. The cover of the desiccator was replaced, but its stopper was first removed, and covered with a watchglass and a clean beaker. The apparatus was now kept all night in a warm place, between 40° and 50° C.; thus the silver when dissolved remained in solution, though the volume was restricted to 2 cm. of solution per gram of nitrate. In the morning the process was found to be complete. After washing down the neck with a few drops of freshly distilled water, the flask was placed in the oven as before. The desiccator was washed with a little water, the washings being tested for silver in the nephelometer; if any had been found it might have been feared that more had escaped, but as no trace was ever found, it was inferred that the long inclined neck had caught all the spray.

Attention is now called to the apparatus for evaporation.[1] The main feature of this was the combined delivery tube for the air current and hood for the protection of the contents of the flask. This hood H with its ingress and egress tubes, I and E, is shown in the diagram (figure 1). The dry air used to sweep out the aqueous and nitrous vapors entered from the purifying train at G, where connection was made by a well-ground joint; passing through the tube I, it escaped into the body of the flask and out through its neck. A side tube, E, was attached to H for connection with a water-pump. The flask rested on a triangle of platinum wire attached to a glass tripod, and the whole was placed in a 1.5-liter beaker which served as the oven. A sand-bath enabled this to be kept at any desired temperature. The cover of the beaker was of sheet copper, pierced with three holes, for the tubes I and E, and for the thermometer. As no nitrous fumes escaped into the oven, this cover remained intact. In the preliminary trials the extra tube Q was lacking, the tube I being extended to take its place. The part which had projected into the body of the flask was treated with hot dilute nitric acid and investigated for silver
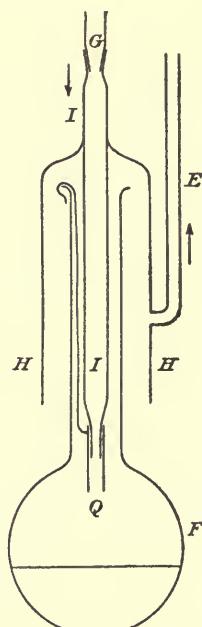
Fig. 1.—Apparatus for Evaporating Aqueous Solutions. Section about half actual size.
F, flask of fused quartz.
H,H, protecting hood, with tube I for air supply.
Q, quartz tube suspended by platinum wire, serving as air-nozzle.

[1] In passing it might be, noted that one of us used a somewhat similar arrangement for evaporating solutions of sodic sulphate fifteen years ago (Proc. Am. Acad., **26**, 258 (1891).

in the nephelometer. Occasionally, some was found, but the corrections required were not large. Nevertheless, the possibility that the fused nitrate had attacked the glass was always disturbing, and the inconvenience and uncertainty of this correction made its elimination desirable. Accordingly, in the final determinations, a section of quartz tubing, Q, 3 mm. in diameter and 15 mm. long, was firmly attached to a platinum wire and lowered till it barely projected into the body of the flask. This supporting wire hooked into the collar, so that the quartz tube could be removed while the silver was dissolving. During the evaporation, however, it was in place, and the end of the glass delivery tube was shortened and drawn down to fit into it. The glass tube was still tested as before, but no silver was ever recovered from it. Hence the flask and the quartz tube must have retained all the silver originally weighed out.

The evaporation of the liquid was easily and quickly conducted in this apparatus. If the flask was not more than half full and the air passed through the drying train no faster than two bubbles per second, it was possible to maintain the temperature of the oven at 125° without risk of ebullition. The vapors drawn out as before described passed first through a U-tube filled with moist glass beads and just sealed with water, afterwards through a tower of caustic alkali to take out nitric acid which might attack the water-pump. When the liquid became coated with a film of crystals the temperature was lowered to 110°; bubbles of vapor now formed gradually under the crystal layer, and the slight spattering caused by their rupture could be seen on the inside walls of the flask. The oven was now suddenly cooled, so that the vapors from the hot liquid, condensing on the walls of the flask, washed down the crust which had formed during evaporation. Upon continuing the heating, a porous crust was soon formed, under which the formation of steam caused no spattering. Finally, the temperature was raised gradually while the last trace of liquid was disappearing. The solid was dried for a quarter of an hour at 150° in the dark, and then heated to 230°[1] to insure complete fusion. not only of the main portion, but also of any portions projected on the upper walls of the flask. The temperature was soon lowered to 210°, which sufficed to keep the mass in fusion, and the air current was continued for an hour. Then, in subdued light, the flask was lifted out by a loop of platinum wire passed through its collar, placed on a network of platinum wire, and tilted in all directions to cause the nitrate to solidify in a thin layer on the walls. Once this precaution was neglected and the flask was cracked by the contraction of the nitrate on cooling.

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[1]This temperature and the others to be recorded later have not been corrected for the exposed steam. They do not indicate the exact meeting-point of the salt.

When the nitrate was wholly solid but still hot, the flask with its contents was transferred to its support of platinum wire in a large, tight desiccator, which was wrapped in a black cloth and left near the balance over night. Then the weight of the flask was determined as before. Thus in the entire cycle of operations nothing but platinum, clean glass, and pure air touched the outside of the flask.

It remains to be proved that no silver was carried out by the air current. This was inferred because no trace of silver was ever found in the U-tube through which all the vapors passed; but more definite evidence was obtained by redissolving two finished determinations, and evaporating them again with the customary precautions.

Determination number.	AgNO₃ once evaporated.	AgNO₃ twice evaporated.	AgNO₃ thrice evaporated.	Total gain.
8	10.68933	10.68928	10.68920	− 0.00013
15	14.20114	14.20122	14.20127	+ 0.00013
Average gain or loss				± 0.00000

The first residue in the case of No. 15 was slightly darkened by prolonged heating; still no fixed tendency toward either loss or gain is shown by these figures, and the reliability of the method is demonstrated.

Two preliminary experiments were not finished, and one was rejected because of known error. Six preliminary determinations carried out in the way just described gave results varying from 157.483 to 157.475 parts of nitrate from 100.000 parts of silver, in the mean 157.479. This is very nearly the same as the final series, given later, but because of sundry irregularities these determinations are individually much less trustworthy than the latter. One of the preliminary determinations was made with a piece of silver kindly given us by Professor Baxter for the sake of comparison, and for which we are much indebted. It gave a result perhaps higher than the average, but not by an amount greater than the limit of error of the experimentation at that time. It is greatly to be regretted that this piece was not examined after every detail of the process had been perfected, because the comparison would have been interesting, although not at all essential for the completeness of our work.

When it appeared impossible to improve upon the details of the experimentation, a final series of six consecutive determinations was carried out with all possible care. In each case, except Nos. 14 and 15, the argentic nitrate was maintained for an hour in a fused condition while dry air swept over it. In No. 14 only one-quarter of an hour was allowed, whereas in No. 15 the fusion was prolonged for three hours. Sample D

of silver was used in syntheses 10, 11, and 12, and sample F in the other three.

The Synthesis of Argentic Nitrate.

No. of synthesis.	Weight of fused silver (in vacuum).	Weight of fused argentic nitrate (in vacuum).	Weight of argentic nitrate made from 100.000 parts of silver.
	Grams.	*Grams.*	
10	6.14837	9.68249	157.481
11	4.60825	7.25706	157.480
12	4.97925	7.84131	157.480
13	9.07101	14.28503	157.480
14	9.13702	14.38903	157.481
15	9.01782	14.20123	157.480
Average...	....	....	[1]157.480

[1] The probable error of this average, computed from the results when carried to the next decimal place, is only 0.0001, a wholly negligible quantity. Hence repetition of the process was unnecessary.

For this ratio just found to be 100.000 : 157.480, Stas obtained an average of 100.000 : 157.475 from nine determinations, which ranged from 157.463 to 157.488.

Better agreement than that exhibited by the above table could hardly be desired or expected, as the greatest deviation corresponded to less than 0.1 mg. in the weight of the argentic nitrate. This series demonstrated that it is not necessary to use very large amounts of material in order to attain a very high order of precision, if only the details of experimentation are fittingly arranged.

Satisfactory as this series of results appears to be, it is by no means to be accepted without further question as representing the true weight of argentic nitrate to be obtained from pure silver. Even in this fused salt, prepared under such favorable conditions, several impurities might exist; and because in each case the method of treatment was the same, these impurities might be constant in amount and therefore not perceivable in the results. Accordingly, attention was now directed to the search for these impurities; and this part of the investigation was found to be the most arduous and time-consuming part of it. The following section discusses this matter.

THE PURITY OF THE FUSED ARGENTIC NITRATE.

The first impurity for which search was made was air. While crystals obtained from solution, although always containing solvent, may be supposed to be free from air, the fused material can not without question be assumed to be free from this impurity. The only manner of approaching this question seems to be to fuse the salt a second time in a vacuum, in order to detect a possible loss of weight. This Stas did in a single case, with a negative result. Nevertheless, a single experiment, even of Stas's, does not carry with it much weight; therefore the test deserves repetition.

This was carried out in the present case without great difficulty on five of the preliminary determinations. The flasks containing the argentic nitrate which had been fused for an hour in air were lowered into mammoth test-tubes — long tubes of soft glass 4.5 cm. in diameter — sealed at the lower end and scrupulously clean. A hood was placed over the mouth of the flask to prevent fragments of glass from entering, and the tube was drawn down in two large converging blast flames. A glass tube was fused on and connected with an efficient mechanical hand pump; several exhaustions, followed by admission of dry air, excluded all moisture. Finally, the system was reduced to 2 mm. and sealed, and heated to 210°. After having been maintained in a state of fusion in the dark for half an hour, the salt was cooled in the usual cautious fashion, and air was admitted very slowly. The flask was placed in a desiccator over night and weighed. The product was always slightly discolored, indicating decomposition, but showed no serious loss in weight.

The Effect of Fusion in Vacuum.

Determination number.	Original weight.	Weight after fusion.	Change.
	Grams.	*Grams.*	
1	8.04489	8.04477	— 0.00012
2	8.75813	8.75810	— 0.00003
3	8.54170	8.54170	± 0.00000
4	9.87850	9.87837	— 0.00013
9	10.76381	10.76374	— 0.00007

Forty-five grams of salt lost in all 0.00035 gram. This is less than 1 part in 100,000, and may safely be referred to the trace of decomposition indicated by the pale-brownish coloration. Not only is it reasonable to suppose that but little air is dissolved (for according to the law of Henry nearly all of it should have been expelled by this treatment) but also one is led to infer that very little water remains to be expelled. This

matter is not, however, so simply settled; the final testing of it cost much labor.

It has been ordinarily assumed that water is entirely expelled from crystallized or evaporated salts upon fusion. This is in all probability the case with sodic and potassic chlorides, and other salts which fuse at high temperatures and show little affinity for water. Whether or not this was the case with argentic nitrate, which at 210° is miscible with water in all proportions, was a question which required experimental investigation.

Besides the conservation of weight on fusion in a vacuum another argument may be adduced to show that most of the water has been driven out. The combining weight of argentic nitrate seems to be nearly independent of the time of its fusion in a current of dry air, as is shown by the following table.

Determination.	Time kept in fusion.	Weight of AgNO₃ formed from 100 parts Ag.
14	15 minutes.....	157.481
9, 10, 11, 12, 13	1 hour............	157.480
15	3 hours..........	157.480

It should be stated that the last residue was slightly discolored, and increased 0.00008 gram upon a subsequent evaporation with water and nitric acid; hence a real loss of weight during the extra period of fusion is indicated; but this was probably due to decomposition of the salt rather than to escape of water; therefore the table bears out the contention stated above. In any case this loss amounts to much less than a unit in the last decimal place.

Ordinarily, in the past, the investigator has been satisfied with such an outcome and has gone no further. But in this case we were anxious to leave no stone unturned; and accordingly a drastic method of treatment was adopted, which permitted no trace of water to escape being weighed. This was to decompose completely the argentic nitrate by heat, and to pass the gaseous product of the decomposition through a weighed tube containing phosphoric oxide.

A hard glass combustion tube was bent and drawn out in the manner shown in figure 2, the space between C and D being packed with glass wool. Into the space between B and C was then introduced about 50 grams of argentic nitrate which had been crystallized from nitric acid, barely fused in porcelain, cooled, and pounded in a mortar. The tube was heated to 220° in an air-bath for an hour in a stream of dry air passed in through A. The argentic nitrate should now be in a condition somewhat comparable to that of the quantitative determination. Finally, a

weighed pentoxide tube was attached at *D*, and the temperature raised to 500°. Yellow oxides of nitrogen came over, also a fine gray dust caused presumably by the bursting of bubbles of decomposing salt. After an hour the pentoxide tube was removed, swept out with air, and weighed again.

Fig. 2.—Tube for Decomposition of Argentic Nitrate, about one-eighth actual size.

A trace of the gray dust had been carried in, and suggested a slight gain in weight, but by no means enough to account for the great increase of weight, 0.012 gram. This was finally traced to the adsorption of nitrous fumes by the pentoxide, 2 mg. being lost upon passing dry air over the tube for an hour, and the rest giving a very strong test for nitrous acid after being dissolved in water.

In the effort to eliminate this seriously disturbing effect, recourse was next had to spirals of copper gauze heated in a combustion tube, in order to abstract the oxygen from the nitric oxide, leaving only nitrogen. It is well known that metallic copper adsorbs hydrogen; hence the spirals were first superficially oxidized in a stream of dry air, and then reduced by pure dry carbon monoxide. This was generated by heating the purest oxalic and sulphuric acids of commerce together, the carbon dioxide being absorbed by a generous train of pure concentrated potash solution, and the monoxide dried first by a tower of concentrated sulphuric acid, with beads, and finally by two towers of pounded potash. The resulting copper should be above the suspicion of containing any considerable amount of hydrogen or moisture. The argentic nitrate was treated as before, and the decomposition was continued until traces of yellow fumes were noted coming past the copper. This meant that nitric oxide had been coming over for some time, since the last part of oxygen is harder to detach than the first. When swept out with air, the gas in the pentoxide tube turned yellow, but it was not then supposed that much nitric oxide could be absorbed by the pentoxide in so short a time. Nevertheless, nitrous acid was found upon solution, even although the gain in weight was only a third as great as before.

Efforts were now made to reduce accidental water from rubber, etc. All joints were made to overlap, so that the rubber surfaces exposed to nitric oxide might be small, and large asbestos screens kept them from being overheated by the adjacent furnaces. Fresh sublimed pentoxide was used in the weighing-tube, which was carefully imitated as to volume and surface by a similar tube, to be used as a counterpoise in weighing; both were opened after coming to the temperature of the balance-room, wiped with a clean, slightly damp cloth, and weighed by substitution. A substantial plug of glass wool in the decomposition tube strained the gases
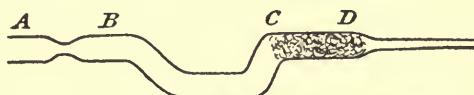
before passing over the copper; it had been heated in the dry air to remove moisture.

To eliminate the possibility of water in the copper gauze and to test the apparatus, a blank run was made, removing the decomposition tube, and oxidizing the copper with dry air. Here the pentoxide tube lost 0.0004 gram, a result which indicated no error in that part of the process.

It is not worth while to record the individual experiments by which the gradual improvements in apparatus and manipulation were tested, tiresome and time-consuming as these were in execution. By the time seven experiments had been performed, it was clear that the fused argentic nitrate could not contain over 0.004 per cent of water. Even of this small amount a part was undoubtedly due to nitric peroxide; for the copper gauze was not enough to effect a complete decomposition of the gases. Passing carbon monoxide through the apparatus while the decomposition was in progress lengthened the effective life of the reduced copper, but introduced other complications; and the addition of a second tube of hot gauze, a meter long, was still inadequate.

The next step was to secure a copper surface so large that all the nitrogen oxide resulting from the complete decomposition of 50 grams of argentic nitrate could be removed, and this without increasing the complications of the apparatus. Powdered copper oxide looked promising as a source of this metal, but it must be made from pure materials to avoid the presence of detrimental impurities. Pure electrolytic copper (Merck) was dissolved in nitric acid, evaporated to dryness in porcelain, and very gradually ignited, with constant stirring, to powdery oxide. A hard glass tube 30 cm. long and 3 cm. internal diameter was used to contain it; the ends were drawn down conveniently and the oxide was reduced at a very moderate heat with carbon monoxide, prepared as usual, except that it was finally dried with pentoxide. Nearly 300 grams of copper oxide were present; therefore, the process was very tedious, since the gas had to pass through its purifying train at a moderate rate of speed. With this large mass of finely divided copper the glass wool (from C to D in the diagram) was no longer necessary, therefore it was no longer used. No trace of powdered nitrate ever appeared beyond the copper.

A clean pentoxide tube, with glass stopcocks, was refilled with resublimed pentoxide and glass wool; dry air was passed through for ten minutes to assure constancy. A duplicate tube was also prepared for a counterpoise, and extraordinary precautions were taken in protecting and weighing these tubes. As another precaution it seemed also expedient to prepare argentic nitrate nearly as pure as that used in the determinations for fear of hygroscopic nitrates, silicic acid, and ammonium salts, which would yield water when decomposed. A moderately pure salt was recrys-

tallized from nitric acid, filtered, precipitated with formate, washed free from ammonium salts, and fused on lime in the blast. The buttons were etched and dissolved in freshly distilled nitric acid in Jena glass, and the salt was crystallized with ample protection against ammonia, dried centrifugally and kept in a clean, tight desiccator. There was no ammonia in this product. Before using it was fused in platinum.

In the first determination of this series the argentic nitrate was heated too hot (520°) and the gases came over so fast that the reduced copper was only superficially attacked; even so it was vastly more efficient than the gauze. Because, however, some nitric peroxide still escaped, this experiment also had to be rejected, a part of the 0.004 per cent impurity which it indicated being undoubtedly due to nitrous fumes.

The apparatus was now improved by sealing off the end (A) of the tube after the argentic nitrate had been fused for a long time in a current of dry air. Moreover, the last trace of rubber exposed to nitrous fumes was eliminated by providing an accurately ground joint between the decomposition tube and the copper oxide. The process was conducted so slowly at 490° that the argentic nitrate could be entirely decomposed to pure spongy silver without exhausting all the copper. Care was taken to have the very pure argentic nitrate in a state comparable to that used in the determinations. The salt after its preliminary treatment in platinum still contained a few crystals of unfused nitrate; accordingly in the tube it was heated evenly at 220° with shaking to dislodge steam bubbles, exactly as the determinations had been. Under these conditions reliable results were obtained. In No. 25, a second weighed pentoxide tube placed in tandem with the first showed no gain in weight; hence the first tube caught all the water vapor. The remaining nitrogen was driven out by pure dry air before weighing. That water vapor was actually present was shown by the "melting" of phosphoric pentoxide in the first tube.

Water Obtained by Decomposition of Argentic Nitrate.

Experiment number.	Weight of AgNO₃.	Gain in weight of drying tubes.	Percentage of water found.
	Gram	*Gram*	*Per cent*
25	53	0.0015	0.0028
26	52	0.0011	0.0020
27	44	0.0014	0.0033
Average...	50	0.0013	0.0027

Thus it is clear that less than 0.003 per cent of water was held by the argentic nitrate after fusion. There was only one other source from which this milligram or so of water might have come, namely, from the

copper used for the reduction of the nitrous fumes. Less than 0.0002 gram of hydrogen retained by 300 grams of copper, or less than one part in a million, would have been enough to cause this effect, hence it seemed rash to assume that the water did not come from this source. As much hydrogen as this might have come from a trace of moisture in the hundred liters of carbon monoxide used for the reduction of the copper.

The question thus raised was capable of being investigated. For this purpose the mass of copper, reduced just as it would have been for one of the preceding experiments, was twice oxidized by a very large volume of pure ignited air dried with the usual potash towers and finally with phosphoric pentoxide. This air, having been already passed over red-hot cupric oxide in a hard glass tube and thoroughly dried by pentoxide, could hardly bring with it any water which could be taken up by the following tube of the same material. On one of these occasions, 0.0009 gram of water was found, and on another 0.0007 gram. Possibly some of this may have come from the atmosphere during the manipulation of the tubes; but a similar amount must be supposed to have been taken during each of the previous determinations. Hence it seems to be permissible to subtract the average 0.0008 gram from the average result of experiments 25, 26, and 27, namely, 0.0013 gram. This leaves only 0.0005 gram as the maximum amount of water held by 50 grams of carefully fused argentic nitrate, introducing an error of only 1 part in 100,000. As the average of the final series led to a value a trifle over 157.480 grams as the weight of nitrate obtainable from 100.000 grams of silver, the correction to be applied for water reduces the result only to 157.479. Possibly not even as much water as this was present in the quantitatively made argentic nitrate, because the relative surface exposed for drying was not so great in the long, narrow tube just used as it was in the quartz flask employed for experiments 10 to 15.

This unimportant change in the synthetic result from 157.480 to 157.479 was the only apparent outcome of these tedious and often exasperating experiments on the decomposition of the nitrate; but in reality more was shown by them. The experience furnished to the experimenters a striking example of the essential importance of taking as much care in determining a small correction as in determining the quantity to be corrected. It moreover confirmed the impression that except in cases like the chloride of zinc, when water acts chemically upon the substance, little or no water is retained by most fused salts. If argentic nitrate, which at 200° is miscible with water in all proportions, sets free so nearly all that it possesses in a current of dry air at this temperature, it is much more likely that other salts, fusing at a higher temperature and possessing a less attraction for water, should be free from it after fusion. This is a reassuring conviction, well worth the trouble spent upon the point.

Attention was now directed to other foreign substances besides water and air which might be present in the synthetic argentic nitrate. Further careful investigation was needed to show that all the silver was combined as nitrate and that no other impurities were concealed in the salt. The pure pearly whiteness of the cold fused material precluded the possibility of there having been a trace of reduction to metallic silver. The salt was soluble in pure water without residue or turbidity, and maintained its clearness when diluted to half or quarter normal; hence oxide and halogen salts must have been absent. The only other likely impurity seemed to be ammonium salts, nitrite, and excess of nitric acid. Of these possibilities, Stas thought only of the likelihood of the presence of free acid; but each was carefully considered in the present work.

It is known that copper dissolving in nitric acid forms perceptible quantities of ammonic nitrate. Apparently, no similar reaction has been noted with silver, and from an electrochemical standpoint it seemed unlikely; moreover, ammonic nitrate if present would probably be for the most part decomposed by the hour's fusion of the silver salt. Nevertheless, thoroughness demanded evidence on this point. Nessler solution is the most convenient for this test, but silver must first be precipitated from solution in the dark. Light generates chlorine which interferes with the test.

In order to prepare for this search for ammonia, the synthetic nitrate of silver resulting from several experiments was shaken with a slight excess of standard pure sodic chloride until the supernatant liquid was clear; the latter was decanted, made up to 50 cc., and placed in a comparison cylinder. The sodic chloride gave no test with Nessler solution.

The cylinder full of liquid prepared from the argentic nitrate was finally tested by comparison with other cylinders containing known traces of ammonic nitrate mixed with sodic nitrate in concentration equal to that existing in the actual determination. The sodic nitrate had been several times recrystallized with centrifugal draining, and was shown to be free from ammonia. In this way the following results were attained: Synthesis 12 was found to contain 0.05 mg. of ammonic nitrate, synthesis 13, 0.06 mg., and synthesis 14, 0.05 mg.; in all, 36.5 grams of argentic nitrate were proved to contain no more than 0.00016 gram of ammonic nitrate — less than one two-thousandth of 1 per cent. The source of this ammonia was not determined; it might have come from the reduction of nitric acid or from the large volume of air used in evaporating the argentic nitrate. The only possible place where it could have entered with the reagents used in the test was in the sodic chloride solution; this was indeed tested, with negative results, but Nessler's reagent is not very sensitive in the presence of chloride, and a trace of ammonia might have eluded detection. If the amount found had been larger, more time would have been spent upon the matter, and a sample of the argentic nitrate often recrystallized

in an atmosphere free from ammonia would have been used in a blank experiment for comparison; but with such a small trace of impurity this was not worth while.

In summing up the results of the test for ammonia, the amount should be calculated for the quantity of argentic nitrate produced from 100.000 grams of silver. Thus it is found that 157.480 grams of fused argentic nitrate could not have contained over 0.0007 gram of ammonic nitrate.

The next impurity to be studied, nitrous acid, was sought by means of sulphanilic acid and naphthylamine hydrochloride. These were proved with a standard nitrite solution of which 1 liter contained 0.1 gram of nitrogen. To insure parallel conditions in testing by comparison, pure silver nitrate was prepared with some care. It was thrice recrystallized from nitric acid with centrifugal treatment, fused in porcelain, then recrystallized three times more from the purest water in platinum, with centrifugal draining as before. The specimens of fused argentic nitrate resulting from quantitative determinations were dissolved in known amounts of water, and comparison solutions of equal concentration prepared. The crystallized silver nitrate gave no trace of pink color with the reagents. A fresh solution to which 0.1 cc. of nitrite solution (0.01 mg.) had been added gave a pronounced color, while determinations 2, 3, and 11 all gave a much fainter, barely visible color; hence it was permissible to conclude that the loss of oxygen from the nitrate on fusion could not have exceeded 0.000005 gram, a wholly negligible quantity.

In seeking for the next impurity, free nitric acid, Stas tested aqueous solutions of his fused silver nitrate with "tournesol" and found them alkaline rather than acid. This alkali may have come from his glass vessels. We used methyl orange, a more sensitive indicator, and noted that the purest crystallized neutral specimens and the fused salt alike gave equally pronounced acid reactions in solution. The color was not modified by the addition of half a milligram of nitric acid; therefore the equality in color does not disprove the presence of free acid in our fused product. Dilute sodic hydroxide freed from carbonate by baric hydroxide threw down a precipitate without changing the pink color. Hence the indicator was discarded and the investigation continued with the nephelometer.

The test for acid with the help of this instrument was conducted by adding a very dilute standard caustic alkaline solution to the solution to be tested and by observing if this addition caused a permanent cloud.

Preliminary trials were necessary in the first place in order to determine the conditions best suited for accuracy. It was found that a concentration of nitrate no stronger than 4 grams in 0.025 liter was best adapted to this work, as argentic hydroxide is distinctly soluble in double this concentration of argentic nitrate. On the other hand, argentic hydroxide precipi-

tated by somewhat concentrated alkali does not quickly redissolve in an equivalent quantity of nitric acid, mixed with the dilute argentic solution. It was found that even the precipitate caused by 0.1 ml. of a two-hundredth normal solution may produce a fairly permanent cloud in spite of the presence of an excess of 0.00003 gram of nitric acid, enough to dissolve it.   Still more dilute solutions behaved much more satisfactorily, however.   A milliliter of a two-thousandth normal caustic solution (equivalent to 0.00003 gram of nitric acid) added with constant stirring to the pure standard argentic nitrate formed a cloud easily seen in the nephelometer.   In case 0.00003 gram of nitric acid had been introduced before adding alkali, no precipitate was formed under the same conditions. Hence under these circumstances the test attained a degree of sensitiveness suited to the case in hand.

In this way it was found that the argentic nitrate remaining from synthesis 11 gave a distinct opalescence with the addition of 0.00002 gram of sodic hydroxide, and an obvious cloud with 0.00003 gram.   Hence it was concluded that argentic nitrate fused in a stream of pure air for one hour contains no weighable excess of nitric acid.

The various suspected impurities having thus been duly sought, it is instructive and interesting to tabulate the results.   These are as follows:

	Grams
Weight of fused AgNO₃ from 100,000 grams Ag.	157.480
Correction for weight of—	
Dissolved air	0.000
Retained water	— 0.0016
Retained ammonic nitrate.	— 0.0007
Nitrite	0.000
Free acid	0.000
Corrected weight of argentic nitrate obtainable from 100.000 grams of pure silver	157.478

As the subtractive corrections given in the above table are maximum values, the weight of argentic nitrate in question can hardly be lower than this value, 157.478.   On the other hand, it can hardly be higher than the uncorrected value, 157.480.   Thus two limits are set, very near together, between which the true value must lie.   Obviously, for the present one can not go very far astray in accepting the mean value, 157.479; and this value will be used in the following discussion.

THE FINAL RESULT AND ITS RELATIONS TO THE VALUES OF ATOMIC WEIGHTS OF NITROGEN AND SILVER.

The conclusion reached by the foregoing series of experiments is that 100.000 parts of silver yield very nearly 157.479 parts of argentic nitrate. Among other experimenters, Penny found 157.442; Marignac found 157.424; Stas found 157.474 in one series of seven determinations and 157.486 in another of two, and Hardin found 157.484. From these older figures, by an interesting coincidence Clarke calculated exactly the value found in the present research.[1] This coincidence is to be attributed not so much to the efficacy of the method of calculation as to the fact that in this case the impurities in the silver happened to balance exactly the impurities in the argentic nitrate. At first sight it is incomprehensible how Stas, working with slightly impure silver, could have obtained any results higher than the true value; but it must be remembered that his nitrate was fused in a glass vessel, which must have been attacked by the strongly acid nitrate at 220°. Constancy in the weight of the vessel would be no evidence of absence of action, for silver might partly take in the glass the place of the sodium taken from it. Thus a gain in weight due to sodic nitrate might be accompanied with no considerable loss of weight of the vessel. In favor of this hypothesis is the fact that Stas's results steadily decreased in each series, as he proceeded with the work; the flask seems to have been less and less susceptible to attack, as is reasonable. If the last two determinations of the first series are taken as the most nearly free from this cause of error, the number 157.466 obtained from them should furnish, by comparison with our number, some clue to the amount of gaseous impurity in Stas's silver. Thus it appears that his silver must have contained nearly 0.01 per cent of impurity — probably more if it is considered that the flask was still not wholly resistant — a conclusion not very different from that reached by Richards and Wells.

Speculations of this kind concerning older work are rather a thankless task, however; there is usually too much that is doubtful to allow them to serve a very valuable purpose. The only object in pursuing the review at all is in order to assure one's self that no real inconsistency exists in the data.

[1]Recalculation of the Atomic Weights (1897), p. 64.

Attention is now directed to a more important matter, namely, the effect of the new experimental result upon the table of atomic weights. This is quickly stated: The newly advocated low atomic weight of nitrogen is incompatible with the ratio 100.000 : 157.479, if silver is taken as 107.930. If on the other hand, the new atomic weight of nitrogen is the true one, silver must have a much lower value than this.

The exact figures are given in the following table:

The Atomic Weight of Nitrogen.

If $Ag = 107.930$, $AgNO_3 = 169.967$ and $N = \mathbf{14.037}$
If $Ag = 107.890$, $AgNO_3 = 169.904$ and $N = \mathbf{14.014}$
If $Ag = 107.883$, $AgNO_3 = 169.893$ and $N = \mathbf{14.010}$
If $Ag = 107.880$, $AgNO_3 = 169.888$ and $N = \mathbf{14.008}$

This series of conditional statements contains in a nutshell the result of the present investigation. In order to decide between the alternatives, other compounds must be further studied, especially the chlorates and the ammonium salts. Investigations in both of these directions have already been begun in the Chemical Laboratory of Harvard College.

SUMMARY.

Argentic nitrate was made from pure silver, and the gain in weight was carefully noted.

In the course of the work, a new and convenient apparatus for quantitative evaporation was devised. Quartz flasks were used as a part of it.

The argentic nitrate was fused until constant in weight; it was carefully tested for dissolved air, retained water and ammonia, and nitric and nitrous acids. Only the second and third of these impurities could be detected by tests proved to be adequate, and these only in mere traces, between 0.001 and 0.002 per cent in all.

` The outcome was that 100.000 parts of pure silver produced 157.479 parts of argentic nitrate. If, then, silver is taken as 107.93, nitrogen must be 14.037; or if silver is taken as 107.880, nitrogen must be 14.008, oxygen being 16.000.

IV

THE MOLECULAR WEIGHT OF ARGENTIC SULPHATE AND THE ATOMIC WEIGHT OF SULPHUR

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BY THEODORE WILLIAM RICHARDS AND GRINNELL JONES

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THE MOLECULAR WEIGHT OF ARGENTIC SULPHATE AND THE ATOMIC WEIGHT OF SULPHUR.

INTRODUCTION.

The atomic weight of sulphur has been investigated by many experimenters; but, as will be seen, the results are far from concordant. A brief review of these investigations forms the most appropriate introduction to the present one. The values in the following list have been recalculated with modern figures for the other atomic weights involved:[1]

1814.	Berzelius (Phil. Trans., **104**, 20)	32.0
1826.	Berzelius (Pogg. Ann., **8**, 15)	32.08
1833.	Turner (Phil. Trans., **123**, 539)	32.00
	Do	32.06
1836.	Thomson (J. prak. Chem., **8**, 370)	32.
1844.	Erdmann and Marchand (J. prak. Chem. **31**, 396) . . .	31.99
1845.	Berzelius (Lehrbuch, 5th ed., **3**, 1187)	32.04
	Do	32.16
1848.	Svanberg and Struve (J. prak. Chem., **44**, 320)	32.15
1851.	Struve (Liebig. Ann., **80**, 203)	31.94
1859.	Dumas (Ann. Chim. et Phys. [3], **55**, 148)	32.00
1860.	Stas[2] (Bull. Acad. Belg. [2], **10**, 153, 322)	32.06
1878.	Cooke (Proc. Amer. Acad., **13**, 50)	32.137
	Do	31.980
1891.	Richards (Proc. Amer. Acad., **26**, 268)	32.043
1898.	Leduc (Ann. Chim. et Phys. [7], **15**, 94)	32.056
1899.	D. Berthelot (Jour. de Phys. [3], **8**, 271)	32.050
1904.	Jaquerod and Pintza (C. R., **139**, 129)	32.01
1905.	Guye (C. R., **140**, 1242)	32.065
1905.	Jaquerod and Scheuer (C. R., **140**, 1384)	32.036

The work of the predecessors of Stas is now of historical interest only and does not merit detailed criticism; in recent times the atomic weight of sulphur has rested chiefly upon the experiments of the famous Belgian.

Stas converted silver into its sulphide by heating it in a current of sulphur vapor or hydric sulphide; but because he did not know the precautions necessary for preparing perfectly pure silver,[3] it is evident that all of his work in which silver was weighed needs revision. Stas also reduced argentic sulphate to silver in a current of hydrogen, but in this case he

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[1] Ag = 107.93; Cl = 35.473; Pb = 206.9; Hg = 200.0; Na = 23.008; C = 12.002.

[2] Van der Plaats, Ann. Chim. et Phys. [6], **7**, 504 and 526 (1886), pointed out that Stas made an error in calculating his own data. Stas obtained 32.074, but 32.06 is correct.

[3] Dumas, Ann. Chim. et Phys. [5], **14**, 289 (1878); Richards and Wells, Publication Carnegie Inst. No. **28**, p. 66 (1905).

did not take the very important precaution of fusing the sulphate before weighing;[1] and moreover, the possibility that the reduced silver might contain argentic sulphide or sulphate was by no means excluded.

A brief review of subsequent work may not be out of place, although it is of a different order of precision. Cooke reduced argentic sulphide in a current of hydrogen, and concluded that the atomic weight of sulphur must lie between the limits 32.14 and 31.98. In summing up his results he stated that "this is equivalent to confirming the accepted value of this constant, so far as any experiments on a scale less extensive than those of Stas can be of value to this end."[2]

The determination of the atomic weight of sulphur by Richards was made incidentally in his work on the atomic weight of copper. The ratio $Na_2CO_3 : Na_2SO_4$ gave as a result $S = 32.075$. If sodium is taken as 23.008 instead of 23.053, the result becomes $S = 32.043$. No very great confidence was placed in these results at the time, as is shown by the following sentence: "The results are hardly capable of deciding the present uncertainty in the atomic weight of sulphur."[3] It is probable that the result is too low, as no proof could be obtained of the thorough desiccation of the sodic carbonate.

Very recently numerous atomic-weight determinations have appeared, depending on a purely physical method, based on the assumption that Avogadro's hypothesis and the simple gas law $PV = RT$ is strictly true for gases when infinitely expanded. Since it is impossible to determine the ratios of the densities of gases with sufficient accuracy at very low pressures, it is necessary to determine this ratio under normal conditions and apply a different correction in each case, depending on the deviation of the gas from the simple gas law. It is probable that the ratio of the densities can be, and in most cases has been, determined with sufficient percentage accuracy. On the other hand, the correction is hypothetical and much less certain; and accordingly, the method has but little value when the correction is large.

According to Leduc[4] the ratio between the densities of sulphur dioxide and oxygen is 2.04835. If no correction is applied for the imperfection of the gases, this value leads to 33.55 for the atomic weight of sulphur. The correction in this case is unusually large and therefore must be known with a high percentage accuracy if the result is to have any value as a determination of atomic weights. The following are the general methods of calculating the correction, but none seems to be of sufficient value for the present case.

[1]Richards, Proc. Amer. Phil. Soc., **42**, 28 (1903).
[2]Cooke. Proc. Amer. Acad., **13**, 52 (1878).
[3]Richards, Proc. Amer. Acad., **26**, 269 (1891).
[4]Leduc, C. R., **117**, 219 (1894).

The first, called the "method of corresponding states" was developed for this purpose by Leduc.[1] It depends on the assumption of van der Waals that two gases are in corresponding states and deviate equally from the hypothetical perfect gas if their temperatures and pressures are equal multiples or sub-multiples of their critical temperatures and pressures, respectively. In calculating the correcting factor, the compressibility and critical constants are used. Leduc[2] by this method obtained 64.056 as the molecular weight of sulphur dioxide, and 34.071 as the molecular weight of hydrogen sulphide, and hence from both $S = 32.056$.

The second method is the "method of critical constants" as developed by Guye.[3] The correction is calculated by the use of van der Waals's equation, the quantities a and b being calculated from the critical constants of the gases under consideration. In a complicated manner Guye applied a correction to the quantities a and b of van der Waals's equation, because they appear to vary slightly with the temperature and the pressure,[4] and in this way was obtained the value 64.065 as the molecular weight of sulphur dioxide; hence $S = 32.065$.

The third method is called the "method of limiting density." It was originated by Daniel Berthelot in 1898[5] and has been used by Rayleigh[6] and Jaquerod.[7] It depends on the experimental determination of the compressibilities of gases at pressures in the neighborhood of one atmosphere. By an extrapolation, the "limiting ratio" of the densities at very low pressures can be calculated. This method has reached its greatest perfection in the hands of Lord Rayleigh, who has shown that for the permanent gases the deviation from Boyle's law only varies slightly with the pressure and therefore the extrapolation is fairly safe. This physical method has been applied with the greatest success to the cases of hydrogen, carbon, and, especially, nitrogen, because in these cases the correction is comparatively small. Here also, however, the application to sulphur is far less satisfactory. It is to be regretted that Lord Rayleigh's work did not include compounds of this element.

Jaquerod and Pintza determined the density of sulphur dioxide at 760 mm., 570 mm. and 380 mm. pressure, and from these results calculated the compressibility. The results were extrapolated to zero pressure on the

[1]Leduc, Ann. de Chim. et Phys. [7], **15**, 5 (1898).
[2]Leduc, Ann. Chim. et Phys. [7], **15**, 94 (1898).
[3]Guye, C. R., **138**, 1215 (1904) ; Bull. Soc. Chim. [3], 5 Août (1905) ; Jour. Chim. Phys., **3**, 321 (1905).
[4]Guye, Bull. Soc. Chim. [3], 5 Août, p. XII (1905).
[5]Berthelot, C. R., **126**, 954, 1030, 1415, 1501 (1898) ; Jour. de Phys. [3], **8**, 263 (1899).
[6]Rayleigh, Phil. Trans. A., **204**, 352 (1905) ; A., **196**, 205 (1901), and A., **198**, 417 (1902).
[7]Jaquerod and Pintza, C. R., **139**, 129 (1904) ; Jaquerod and Scheuer, C. R., **140**, 1384 (1905).

assumption that the deviations from Boyle's law diminish as the pressure is lowered. They obtained 32.01 as the atomic weight of sulphur. Afterwards Jaquerod and Scheuer determined the compressibility of sulphur dioxide through the ranges 400 to 800 mm. and 200 to 400 mm. by a method similar to Lord Rayleigh's. They found, as was to be expected, that the deviation from Boyle's law was smaller at the lower pressure. Nevertheless, in calculating the molecular weight of sulphur dioxide, they assumed that the deviation from Boyle's law per centimeter of pressure between 0 and 760 mm. was the same as between 400 and 800 mm. They obtained 64.036 for sulphur dioxide and hence $S = 32.036$. If their measurement of the compressibility through the range 200 to 400 mm. is used, the result becomes 32.052, and it seems probable that yet a higher value is the true outcome of their experiments. These different conclusions emphasize the uncertainty of the method.

Probably the adsorption of sulphurous oxide and hydric sulphide on the glass of the containing globes introduces an error in both the density and compressibility determinations, and hence in facts to which the assumption above mentioned are applied. This possibility of adsorption seems to have been not sufficiently heeded by any of the experimenters on sulphur compounds. It adds yet another uncertainty to the results.

The upshot of these considerations is the conclusion that none of the work heretofore done upon the atomic weight of sulphur decides its value. Hence further investigation is imperative. The problem, for complete solution, must be approached from many sides, and the work must involve many compounds of sulphur. The following contribution describes one section of a comprehensive program by which it is hoped the question may be answered.

PRELIMINARY EXPERIMENTS.

The sulphate of silver was selected as the most suitable starting-point for the present investigation, because it seemed probable that this salt could be prepared in a pure condition and accurately analyzed. A further reason for studying argentic sulphate lies in the possibility of later combining the results with some ratio involving the sulphide and thus furnishing evidence on the even more important question as to the atomic weight of silver. Balanced against the advantages is the disadvantage that only about 10 per cent of its weight is sulphur, causing the experimental errors to be greatly multiplied in the calculations; but the advantages more than outweigh the disadvantage.

A tentative preliminary plan of operations was to fuse argentic sulphate in a platinum crucible, dissolve it, precipitate as chloride, and collect and weigh the precipitate. This plan was thwarted by numerous obstacles.

It was found that the sulphate decomposes slightly when fused, a difficulty which was later overcome. Again the quantitative solution of the silver sulphate was a very tedious process. Eight grams fused in a platinum crucible and placed in 1.5 liters of water required six weeks for its complete solution, even with frequent agitation. The action on the glass during this long time, the danger of the access of gaseous impurity, and the loss of valuable time all made this difficulty a serious one.

Argentic sulphate can be readily dissolved by placing twice its weight of concentrated sulphuric acid in the crucible and heating at about 300°; on cooling, the acid sulphate of silver crystallizes out.[1] Upon adding water to this acid sulphate the normal sulphate is formed as a fine powder, which can readily be washed into the precipitating flask and dissolved. The large excess of sulphuric acid thus introduced was far from desirable, however, for it tends to cause considerable occlusion of argentic sulphate in the precipitated chloride. In order to test this question, a solution, prepared as described above, and containing 7.4 grams of argentic sulphate, was precipitated with hydrochloric acid. The precipitate was washed by decanting eleven times with very dilute hydrochloric acid and then dissolved in ammonia and diluted. The argentic chloride was then reprecipitated with hydrochloric acid; the solution should contain all the sulphate previously occluded. After settling, this mixture was filtered, and the perfectly clear solution was evaporated in a platinum dish over an alcohol lamp until ammonic chloride crystallized out on cooling, the volume being then about 0.1 liter. To this were added about 10 grams of baric chloride. An undoubted precipitate of baric sulphate was produced, which proved that there is considerable occlusion of sulphate by argentic chloride precipitated from solutions containing a large excess of sulphuric acid.

For the sake of comparison, approximately the same amount of argentic chloride prepared from nitrate was dissolved in ammonia, and 3.5 mg. of sulphate added. The solution was treated exactly like the preceding operations, and yielded about the same amount of precipitate. This experiment gives an approximate idea of the extent of the occlusion.

In searching for a means of wholly eliminating the sulphate it was found that a small proportion of argentic sulphate in argentic chloride could be completely converted into chloride by fusion in a current of hydrochloric acid gas. This observation led to the development of a new process in which the entire reaction was carried out in this manner, fused argentic sulphate being wholly converted into chloride without the need of dissolving in water. Thus the operation was greatly simplified, and the chances of error diminished.

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[1]Schultz, Pogg. Ann., **133**, 143 (1868).

The method of preparing the materials, the shape and nature of the apparatus, and many of the precautions and details of manipulation were adopted only after numerous preliminary experiments. A detailed account of this tentative work is, however, unnecessary, since the important results are implied in the description of the method which was finally adopted.

THE PREPARATION OF PURE MATERIALS.

SULPHURIC ACID.

The best commercial "chemically pure" acid was twice fractionally distilled, using a quartz condenser and a platinum dish as receiver. Only the middle fractions were used; 17 grams left no visible or weighable residue on evaporation.

ARGENTIC SULPHATE.

Pure argentic chloride residues from previous atomic weight investigations in this laboratory were reduced with invert sugar and sodic hydrate. The reduced silver was thoroughly washed, and dissolved in nitric acid; and the nitrate was diluted and filtered. It was evaporated on the steambath until saturated, and crystallized by adding an equal volume of concentrated nitric acid and cooling. The crystals were drained centrifugally as usual.[1] The crystallization from pure concentrated nitric acid and centrifugal draining was repeated five times, using Jena-glass vessels. It was finally recrystallized once more, using a platinum dish and redistilled nitric acid. This silver nitrate was dissolved in a small amount of water in a platinum dish, and an excess of the purest sulphuric acid, diluted with an equal volume of pure water, was poured into it. The precipitated silver sulphate was drained in the centrifugal machine. It was then dissolved in hot concentrated sulphuric acid in a platinum dish, and the solution was boiled for several minutes to expel nitric acid. On cooling, the acid sulphate crystallized in large crystals. This acid sulphate was very thoroughly whirled, placed in a platinum dish, and treated with purest water. Heat was evolved and the normal sulphate crystallized out as a fine powder. This powder was washed by decantation with the purest water until the wash-waters were no longer acid.[2] All the water used in this work was purified in the manner described in previous communications. During this washing the action of light on the wet silver sulphate produces a slight violet color. This, however, does no harm, as any slight decomposition is remedied during the subsequent fusion. It was then

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[1]Richards, J. Amer. Chem. Soc., **27**, 104 (1905).
[2]Unless this precaution is taken the silver sulphate can not be dried thoroughly in the air-bath; in which case it would be impossible to clean properly the receiving end of the tube into which it was afterwards introduced. (See p. 76.)

dried as much as possible in the centrifugal machine, and the drying was completed in an air-bath at 110°. These operations were carried out as much as possible under the protection of a very large inverted funnel, and the dish was kept covered with a large watch glass, to avoid the introduction of dust. This sample was called A and was used in the preliminary series and in experiments 4 and 5 of the final series of quantitative experiments.

Sample A was dissolved in concentrated sulphuric acid, boiled, crystallized as acid sulphate by cooling, centrifugally drained, converted into the normal sulphate by adding water, washed, and dried as before. This sample was called sample B. Since the mean of the results with this sample is the same as the mean of experiments 4 and 5, in which sample A was used, it is evident that the boiling of the sulphuric acid solution followed by a crystallization in two different crystalline forms did not affect the result; therefore further purification seemed unnecessary.

HYDROCHLORIC ACID.

Hydrochloric acid, which was only used as a gas, was made from two sources. In experiments 5 and 6 the hydrochloric acid was made by dropping pure sulphuric acid on pure ammonium chloride. In the other experiments the best commercial concentrated hydrochloric acid was used. Richards and Wells[1] have shown that this acid contained no other halogen or arsenic; it was therefore suitable for our purpose.

THE FUSION OF ARGENTIC SULPHATE.

Much thought was expended on the devising of a piece of apparatus which should be suitable not only for the fusion of argentic sulphate, but also for the quantitative conversion of the sulphate into the chloride. Finally the simple symmetrical tube shown in the diagram was found to be
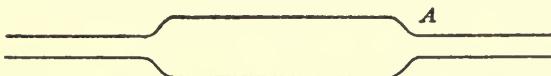

Fig. 3.—Quartz tube used to contain the argentic salts. One-half actual size.

best. It was the outcome of several trials and suggestions, and consisted of a thin cylindrical tube of fused quartz with smaller quartz tubes fused upon the ends.[1] The tube was very light, weighing less than 6 grams. A very fine platinum wire was wrapped many times around the constricted

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[1] Richards and Wells, loc. cit.

[2] We are greatly indebted to Professor Baxter for his kindness in making this apparatus from a fine quartz tube and a quartz test-tube. To Mr. F. B. Coffin also we are indebted for a suggestion which led to a modification of the original shape of the tube.

portion of the tube (A); by pulling this the tube could be readily rotated. It was hung on the balance in a horizontal position by means of a platinum wire. The same tube was used throughout the research, the cylindrical shape giving it sufficient strength to withstand all the strains to which it was subjected.

The tube remained remarkably constant in weight in spite of the very vigorous treatment it received. During the entire fifteen experiments the loss in weight was only 0.41 mg., and during the twelve experiments of the final series the loss was only 0.16 mg. This slight loss is probably accounted for by a slight solubility of the quartz in the concentrated ammonia or potassic cyanide solution used to remove the argentic chloride after each determination.

The sulphate of silver prepared as described above must have contained a little included water and excess of sulphuric acid, since it had been crystallized from an acid solution.[1] The only certain method of removing mother liquor included within crystals is to fuse the salt. This part of the problem caused considerable difficulty; for it was found that argentic sulphate decomposes slightly when fused in air, becoming yellowish-brown in color. In order to decrease this thermal dissociation, the experiment was made of fusing the salt in a current of dilute sulphuric oxide, with complete success. The salt is then pure white in color.

The small crystals of argentic sulphate were pushed into the tube with a platinum rod, and the narrow ends were freed from loosely adhering argentic sulphate by means of a clean feather tip, which had been previously washed with alcohol and ether to free it from grease. The tube was supported, on hooks of hard glass, in front of the apparatus for delivering sulphur trioxide. The very fine platinum wire needed for rotating it had been wound around the tube in the first place.

The apparatus for delivering a current of pure dry air or sulphur trioxide or hydric chloride is shown diagramatically in figure 4. A current of air was first driven over red-hot copper oxide (A) to remove organic matter, and subsequently through an Emmerling tower (B) containing beads moistened with a strong caustic potash solution. This tower was closed by a rubber stopper at the top, which introduced no impurity, since nothing but pure air passed over it. From this point, however, the apparatus contained no rubber connections or stoppers. All stopcocks were lubricated with phosphoric or sulphuric acid.

The air was dried by passing through two Emmerling towers $(C$ and $D)$ containing beads moistened with concentrated sulphuric acid. The cur-

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[1]Richards, Proc. Amer. Phil. Soc., **42**, 28 (1903).

rent of air could then be either used in a pure dry state by passing through L or F, or else charged with sulphur trioxide by bubbling twice through fuming sulphuric acid in the bottle E. This acid was kept saturated by an excess of solid sulphur trioxide. A current of air mixed with any desired proportion of sulphur trioxide was thus delivered through G into the quartz tube H. The delivery tube (G) and the quartz tube (H) touched each other, but no attempt was made to secure a tight joint.
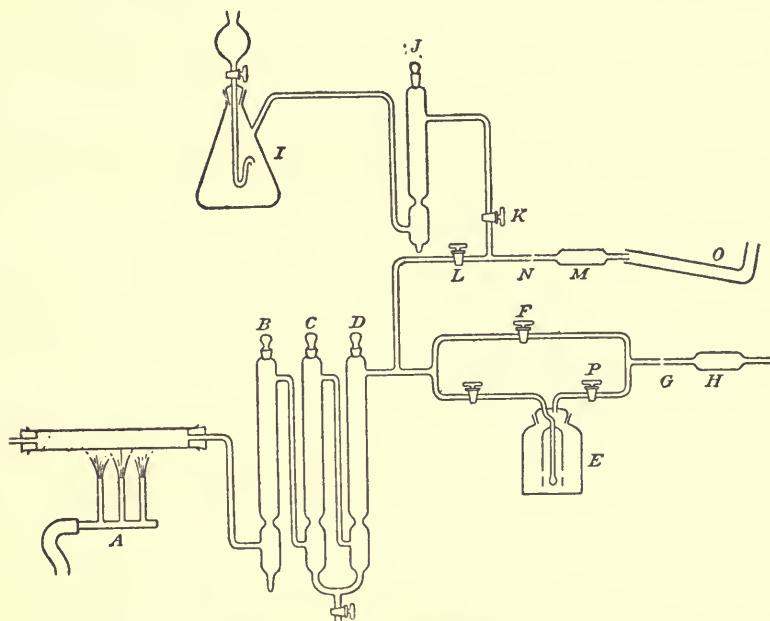

Fig. 4.—Apparatus for delivering appropriate gases into the quartz tubes.

The argentic sulphate contained in the quartz tube was then fused with a fish-tail Bunsen burner held in the hand. A red heat is required. When all of the sulphate was fused, the stopcock (P) delivering sulphur trioxide was closed and a rapid current of air was admitted through F. As soon as the fumes of sulphuric acid could no longer be seen escaping from the end of the quartz tube, the flame was removed and the tube was slowly rotated by drawing out the platinum wire wrapped around one end. This causes the argentic sulphate to solidify in a thin sheet around the tube. Unless care is taken to keep the salt at least 1 cm. distant from either of the end tubes, difficulty is experienced during the conversion into chloride.

The final solidification in the current of pure dry air was carried out very rapidly, in order to avoid decomposition and obtain a perfectly white

sample. If the argentic sulphate was kept fused 10 or 15 seconds too long after the sulphur trioxide current was stopped, a yellowish-brown product was obtained. This indicates that the salt contained either metallic silver or argentic sulphide. Richards, Wells, and Forbes[1] have shown that a slight discoloration of a fused silver salt is a very delicate test for impurity. The loss of weight due to this discoloration was very slight, as will be shown on page 79.

The entire tube was later heated in a current of pure air at a temperature above the boiling-point of sulphuric acid for about 5 minutes, in order to drive out any possible accidental trace of acid in the tube. While still warm it was placed in a desiccator, and later weighed. The tube was kept horizontal until the end of the experiment, to avoid any chance of mechanical loss.

The device of spreading the salt in a thin layer around the tube by rotating the tube during the cooling had four very important advantages: First, the chance of breaking the very fragile quartz tube during the solidification and cooling was greatly reduced by the more even distribution of the strain; secondly, the salt was agitated and spread out in a thin layer while still fused in a current of pure air, thus facilitating the escape of any possible trace of dissolved sulphur trioxide; thirdly, the cooling was made more uniform and rapid, so that the argentic sulphate had no time to decompose before it had solidified; and fourthly, a much larger surface was exposed to the later action of the hydrochloric acid.

The possibility just mentioned that the colorless argentic sulphate might contain an excess of sulphur trioxide needed careful consideration. Unfortunately a direct test for acid seemed to be impracticable, owing to the slight solubility of silver sulphate, hence light upon the question was sought in several distinct ways.

Weber[2] has found that in order to prepare a compound $Ag_2S_2O_7$ argentic sulphate must be heated with sulphur trioxide under pressure in a sealed tube. This, together with the fact that argentic sulphate decomposes so easily when fused, indicates that it does not have a great tendency to retain sulphuric oxide, and that the vapor tension of the trioxide in the disulphate is far above that maintained in the present experiments. In order to obtain quantitative evidence, the pure white sulphate in six of the final experiments, after being weighed, was fused again for about 10 to 15 seconds in order to decompose it slightly. This gave a slight but unmistakable dark color to the salt. The resulting losses of weight are tabulated on page 79.

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[1]Richards and Wells, Carnegie Inst. Pub. **28**, 31 (1905) ; Richards and Forbes, the present publication, p. 55.
[2]Weber, Ber., **17**, 2503 (1884).

The Loss of Weight Caused by Slight Decomposition.

No. of experiment.	White Ag_2SO_4.	Darkened Ag_2SO_4.	Difference.
9	5. 27714	5. 27709	0. 00005
10	5. 16313	5. 16302	0. 00011
11	5. 08383	5. 08377	0. 00006
12	5. 13372	5. 13367	0. 00005
13	5. 16148	5. 16138	0. 00010
15	5. 37436	5. 37425	0. 00011
Average...	....	....	0. 00008

The loss in weight was thus on the average only 0.08 mg. or 0.0015 per cent. In seems certain that at least part of this loss in weight was due to a deficiency of either oxygen or sulphur trioxide in the darkened sulphate, and not to the loss of an illegitimate excess of the latter substance. Therefore, although it may be a debatable question as to whether it is safer to take the weight of the white or darkened samples as the true weight, it seems probable that the weight of the white sample was more trustworthy. Even at the worst the uncertainty can not have been greater than 0.001 per cent. This result agrees with the earlier conclusions already cited concerning the obvious effect of very slight decomposition on the color of silver salts. It appears that in the present case, as in the others, the slight stability of these compounds is a real assistance in the production of a typical compound, instead of a hindrance to precise quantitative work.

For weighing the argentic sulphate, and of course the chloride also, the Troemner balance which had served in many similar researches was used.[1] The Sartorius platinized brass weights were standardized by the usual Harvard method.[2]

As usual, all weighings were made by substitution, a make-weight being placed on the right-hand balance pan. In order to avoid as far as possible any error due to changing meteorological conditions, a substituting counterpoise of the same material and approximately the same surface and weight was used. Every weighing was repeated, and the successive values seldom differed more than 0.03 mg. No difficulty was experienced from hygroscopic adsorption of water by either argentic sulphate or argentic chloride, except on a few days when the air was unusually humid. In these cases the tube was heated to about 330° and allowed to remain in a desiccator until the conditions were more favorable. The tube was always allowed to remain at least three hours in a desiccator near the balance

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[1]Richards, Proc. Amer. Acad., **26**, 242 (1891).
[2]Richards, J., Amer. Chem. Soc., **22**, 144 (1900).

before making a weighing and during this time was covered by a black cloth to protect the sensitive salts from the light.

In order to correct the weights to the vacuum standard, the specific gravity of argentic sulphate is needed. Following are the published results concerning this datum:

Density of Argentic Sulphate.

5.341.	Karsten, Schweigger's J., **65**, 419 (1832).
5.322.	Playfair and Joule, Mem. Chem. Soc., **2**, 430 (1845).
5.410.	Filhol, Ann. Chim. et Phys. [3], **21**, 417 (1847).
5.425.	Schröder, Pogg. Ann., **106**, 245 (1859).
5.49. 5.54. }	Petterson, Upsala, Nova Acta [3], **9**, 35 (1874).

After a study of the original papers, the value 5.45 was provisionally adopted as the most probable value; but, as there was some doubt about its accuracy, this was verified by experiment.

The density of the toluol to be displaced by the salt was determined by means of an Ostwald pycnometer at 29.2° to be 0.8566 (the mean of 3 concordant determinations); 6.067 grams of previously fused silver sulphate were found to displace 0.9532 gram of this toluol, and therefore occupied 1.113 ml. (the mean of two determinations). Hence the density of argentic sulphate is 5.45, as supposed. This involves an additive correction of 0.0000775 gram to each apparent gram of the salt, a value which is decreased 0.0000011 by an increase of a centimeter of atmospheric pressure, or decreased 0.00000026 by an increase of a degree of temperature. The correction to the weight was applied accordingly.

THE CONVERSION OF ARGENTIC SULPHATE INTO CHLORIDE.

The next step in the process was the conversion of the carefully weighed fused sulphate into chloride by heating it in a current of dry hydrochloric acid gas. This reaction has been observed by Hensgen.[1]

The hydrochloric acid generator used for the previous work was constructed entirely out of glass. Pure ammonic chloride or concentrated hydrochloric acid was placed in the flask (*I*) shown in figure 4, and concentrated sulphuric acid was dropped upon it slowly. The gas was dried by passing through the tower (*J*) containing beads moistened with concen-

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[1]Hensgen, Recueil des Travaux chimiques de Pays-Bas., **2**, 124 (1883). "Le sulfate d' argent absorba 2 mol. HCl à la température ordinaire, avec un dégagement de chaleur notable, et se changea complètement en chlorure. En chauffant, même jusqu a 300°, la réaction inverse (observée par M. H. avec le sulfate de cuivre) n'eut point lieu, mais l'acide sulphurique fut chassé complètement par un courant d'air. Parmi les sels susdits, le sulfate d'argent est celui qui d' après les données thermiques, doit se changer en chlorure avec le plus grand dégagement de chaleur." (See p. 83.)

trated sulphuric acid.[1] The gas then passed through the stopcock (K) to the delivery tube (N). The ground-glass stopper at the top of the tower (J) acted as a safety-valve when the stopcock (K) was closed. Pure dry air might also be delivered at N by means of the stopcock (L), in order to sweep out the excess of acid at the conclusion of the reaction.

The quartz tube containing the argentic sulphate was supported by means of hooks of hard glass in front of the delivery tube (N), as before, without making a tight joint.

In seven of the final experiments a condenser tube of quartz (O) was placed over the exit end of the tube (M) in order to condense the sulphuric acid and retain any silver which might escape. As will be shown, only very small traces of silver were found in the distillate. The condensation of sulphuric acid in the narrow tubes on the end was prevented by keeping them hot by means of a small fixed fish-tail burner.

A slow current of hydrochloric acid was generated and the tube warmed gently. The reaction took place readily and quietly, the only difficulty being that the argentic chloride formed was inclined to creep over the walls of the vessel. This was probably due to the liberated sulphuric acid having dissolved undecomposed argentic sulphate; the acid sulphate was then transported by surface tension and converted into chloride in another place. In two of the experiments one of the narrow end tubes was completely blocked up in this manner, making a successful completion of the experiment impossible; but in other cases the difficulty was avoided by starting with the argentic sulphate in a band in the middle of the tube.

The sulphuric acid must be evaporated at a temperature below its boiling-point in order to avoid loss by the projection of small particles. The tube was heated by a flame held in the hand, the heating being regulated by watching the escaping fumes of acid and also the color of the argentic chloride in the tube. It is well known that as the temperature increases, silver chloride acquires a deeper and deeper yellow color; and after acquiring the necessary experience, this change of color proved very helpful in regulating the temperature.

After from 2.5 to 4 hours no more fumes of sulphuric acid could be seen issuing from the tube. The argentic chloride was then fused very slowly and quietly and kept in the fused state for 20 minutes in a current of hydrochloric acid. The tube was gently agitated in order to expose a fresh

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[1]In one of the preliminary experiments the hydrochloric acid was not dried. The sulphuric acid first formed absorbed considerable water, thus becoming diluted and nearly filling the tube with liquid sulphuric acid in which a large part of the silver sulphate dissolved. After heating for some time, the whole mass was solidified. This gave a non-porous mixture of silver sulphate and chloride. The hydrochloric acid had no appreciable further action until the mixture was fused, and then the action became very vigorous. The sulphuric acid which was formed boiled, and caused spattering and therefore danger of mechanical loss.

surface, at intervals of about 1 minute, by grasping the exit end with platinum forceps. The agitation can be performed without danger of loss, because of the high surface tension of fused argentic chloride. This material when liquefied does not adhere to quartz, and therefore is not drawn into the end tubes by capillarity. At the expiration of 20 minutes the current of acid gas was stopped by means of the stopcock (K), and a current of pure dry air was passed through the tube through L, the argentic chloride being still maintained in the liquid state for at least 5 minutes with occasional agitation. The tube was rotated while subsequently cooling in a similar manner to that employed with the sulphate.

The condensed sulphuric acid evolved by the reaction and the condenser tube were tested for silver by means of the nephelometer.[1] The acid was transferred to a small flask and the tube was rinsed with ammonia, which was added to the acid. The excess of ammonia was then neutralized with nitric acid, and hydrochloric acid was added to precipitate any trace of silver present as an opalescent cloud of argentic chloride. This opalescence was compared in the nephelometer with a standard which had been made in a manner very similar to the unknown solution.[2] A measured volume of a standard silver solution was taken; to it were added approximately the same amounts of sulphuric acid, ammonia, and nitric and hydrochloric acids as were present in the unknown solution; and it was made up to the same volume (about 30 ml.).

The greatest amount of argentic chloride thus found in any experiment was 0.00009 gram and the average amount 0.00004 gram. The trace found in this way was of course added to the weight of the silver chloride. In three of the experiments (Nos. 4, 5, and 7) this determination was not made, but the average amount is added in these cases. The probable reason for the escape of this trace of silver will be discussed later.

The question as to whether or not this reaction is complete is, of course, of fundamental importance. There are four pieces of evidence bearing on this point.

In the first place, the argentic chloride was fused for twenty minutes in a current of almost pure hydrochloric acid. Since the temperature was far above the boiling-point of sulphuric acid, this product of the reaction was driven off as fast as formed. Therefore according to the law of concentration-effect it is to be expected that through the agency of the continually renewed hydrochloric acid all the argentic sulphate would be decomposed and all the sulphuric acid would be driven off. This would be hastened by the fact that fresh surfaces were continually exposed through agitation.

[1]Richards and Wells, Amer. Chem. Jour., **31**, 235 (1904).
[2]Richards, Amer. Chem. Jour., **35**, 510 (1906).

Again, in this case the law of concentration-effect is assisted by the relative affinity, indicated approximately by the large amount of heat evolved by the reaction. It can be calculated from Thomsen's data that the reaction gives out 40,400 grams calories,[1] or 170 kilojoules. Rarely, if ever, is the difference between total-energy and free-energy changes in a reaction of this kind as great as this, hence it is safe to infer that there is a considerable preponderance of driving tendency in the desired direction, arising from the mutual affinities concerned.

Thirdly, constancy of the weight on continued treatment indicated the completion of the reaction. In seven of the experiments the argentic chloride was fused a second time in hydrochloric acid for 15 minutes with occasional agitation, followed by 5 minutes in air. The following table gives the changes in weight found in this way:

The Effect of Continued Treatment with Hydrochloric Acid.

No. of experiment.	AgCl, first weighing.	AgCl, second weighing.	Difference.
6	4.67812	4.67809	− 0.00003
7	4.93119	4.93118	− 0.00001
11	4.67373	4.67375	+ 0.00002
13	4.74491	4.74489	− 0.00002
14	4.77995	4.77990	− 0.00005
15	4.94088	4.94088	+ 0.00000
Average...			− 0.000015

The constancy in weight was thus entirely satisfactory, the average loss being only 0.0003 per cent of the weight of the chloride.

This experiment, however, does not absolutely preclude the possibility that a small but constant amount of sulphate may remain. In order to test this question 4.90 grams of argentic chloride which had never been contaminated with sulphate was fused in the tube, and then 0.00479 gram of pure argentic sulphate was added and thoroughly mixed with the chloride by fusion. On cooling the appearance was very different from the pure

[1] Thomsen, Thermochemische Untersuchungen:
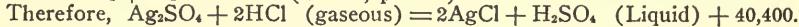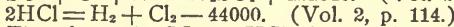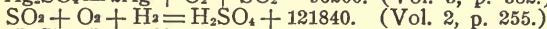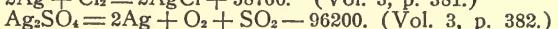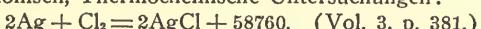
$2Ag + Cl_2 = 2AgCl + 58760.$ (Vol. 3, p. 381.)
$Ag_2SO_4 = 2Ag + O_2 + SO_2 − 96200.$ (Vol. 3, p. 382.)
$SO_2 + O_2 + H_2 = H_2SO_4 + 121840.$ (Vol. 2, p. 255.)
$2HCl = H_2 + Cl_2 − 44000.$ (Vol. 2, p. 114.)
Therefore, $Ag_2SO_4 + 2HCl$ (gaseous) $= 2AgCl + H_2SO_4$ (Liquid) $+ 40,400.$
A different set of equations gave 40,200. The result, of course, only applies to 18°. In this connection it is worth while to note that $Ag_2SO_4 + Cl_2 = 2AgCl + SO_2 + O_2 − 37440$ cal.; which indicates that chlorine would not be as suitable for our purpose as hydrochloric acid. This expectation is confirmed by the experience of Krutwig, Ber., **14**, 306 (1881): "Die Einwirkung ist hier (chlorine on silver sulphate) keine direkte; nur bei sehr hoher Temperatur, nachdem das Salz geschmolzen ist und sich zersetz, giebt es schweflige Saüre, Chlorsilber und Sauerstoff ab."

chloride, the mass being translucent or almost opaque, instead of transparent. It was then fused in a current of hydrochloric acid for twenty minutes after the sulphuric acid could no longer be seen escaping from the tube, as before. On the assumption that the sulphate was converted completely into chloride the loss in weight would have been 0.00039 gram, while the actual loss in weight was 0.00044 gram. The reaction was evidently complete, and a fourth argument was added to the other reasons for believing that the process should yield satisfactory results.

It will be recalled that the narrow end tubes were kept very hot by small stationary burners in order to prevent the condensation of sulphuric acid. At the close of several of the experiments a very slight sublimate was observed on the portion of the narrow tubes which was kept somewhat cooler by the protection of the supporting hooks. This sublimate, although never large in amount, appeared largest in experiments 6 and 10. There was a smaller amount in experiments 7, 11, and 14, but none worthy of consideration in experiments 4, 5, 12, 13, and 15. In experiments 10 and 14 a slight amount of the sublimate was visible in the condenser also, near the end of the tube.

Although the most rational explanation of this trace of sublimate, which was usually too slight to be weighable, was probably to be found in the assumption that it was argentic chloride and therefore entirely without sinister meaning except as suggesting the risk of the loss of other traces, the matter was studied further. Careful tests for arsenic[1] and copper were made with negative results, and the hydrochloric acid was demonstrated to contain no trace of anything which could be deposited in a red-hot quartz tube. On the other hand, the sublimate was soluble in ammonia and behaved in every way like argentic chloride, so that its nature was considered as nearly proved as was possible with such a minute amount of material. Having settled the nature of the sublimate, its source and significance must be traced. Evidently it could not have come from the main body of the silver sulphate, because it appeared at the very beginning of the experiment, as soon as the current of hydrochloric acid was started and the end tubes heated, before the heat was applied to the main body of the argentic sulphate. Moreover, the mass of the argentic chloride was never heated to a temperature high enough to volatilize weighable amounts of this substance, as was shown by the constancy of weight on continued heating in a current of gas.[2]

In view of these considerations, it seemed probable that a few invisible crystals of argentic sulphate had been left in the end tubes by the feather

[1]This test was kindly made by Mr. O. F. Black.
[2]See the preceding description; also Richards and Wells, loc. cit., p. 60; Baxter, Proc. Amer. Acad., **41**, 83 (1905).

used in cleaning it, or carried into the end tube by the current of sulphur trioxide before fusion. As soon as the hydrochloric acid was admitted and the end tubes heated, these small invisible crystals of silver sulphate must have been at once converted into chloride and sublimed to the cooler portion of the tube — for the end tubes were usually raised to a red heat. This explanation is consistent with the frequent absence of any significant sublimate, especially in the case of experiment 15. In this experiment the tube had been dusted and treated with particular care, in order to test the point.

Because the sublimate was weighed in the tube which had previously contained the sulphate, its presence could not affect the accuracy of the results even if it had been weighable. Nevertheless the suggestion that another portion might have been carried out of the tube was worth considering. Doubts on this point were set at rest by the analysis of the contents of the condenser tube which received the volatile products of the reaction. The average amount of silver found in this tube was less than 0.001 per cent of that taken in each experiment, and the small appropriate correction was easily applied.

Although it was not probable that argentic chloride which had been fused in air for five minutes still retained any dissolved hydrochloric acid, this point also was tested. In experiment 13, the silver chloride after the first heating in hydrochloric acid and fusion in air for five minutes as usual, weighed 4.74491 grams. After the second fusion in hydrochloric acid, and finally in air, the weight was 4.74489 grams. After another fusion for twenty minutes in a current of pure air, the weight was 4.74493 grams. These slight changes in weight can only be ascribed to errors in the weighing; the outcome shows that the argentic chloride after the usual treatment did not retain any dissolved hydrochloric acid. Richard and Wells have already shown that it does not dissolve weighable amounts of air.[1]

In still another case the outside of the tube was washed with water to make sure that nothing had deposited on it during the long exposure to the flame and acid. The loss in weight was only 0.02 mg., which again is not greater than the possible error in weighing.

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[1] Richards and Wells, loc. cit., p. 60.

THE FINAL RESULTS.

Having shown the feasibility of the plan of operations and gained practice by three preliminary experiments, a final series was undertaken, whose outcome is detailed below.

Sample A of argentic sulphate was used in experiments 4 and 5 and sample B in the remainder. In experiments 5 and 6 the hydrochloric acid was generated from ammonic chloride, and in the other experiments from concentrated hydrochloric acid. The corrected weight of argentic chloride was obtained by adding the trace found in the condenser to the average weight after fusion in hydrochloric acid. In experiments 4, 5, and 7 the correction for the argentic chloride in the condenser was not determined directly, but the mean of the other determinations (0.00004 gram) was added.

In experiments 8 and 9 the narrow exit tube became completely blocked by the creeping of the argentic chloride. This made it necessary to fuse the solid while there was still present considerable argentic sulphate; and therefore the sulphuric acid boiled and material was lost by being projected out of the tube. The first of these was rejected, and the second not finished. All the other determinations are recorded in full in the table. The weighings have of course been corrected to the vacuum standard.

The Quantitative Conversion of Argentic Sulphate to Chloride.

No. of experiment.	Weight of colorless Ag_2SO_4 in vacuum.	Weight of total AgCl in vacuum.	Parts of AgCl obtained from 100.000 parts of Ag_2SO_4.
4	5.21962	4.79859	91.934
5	5.27924	4.85330	91.932
6	5.08853	4.67810	91.934
7	5.36381	4.93118	91.934
10	5.16313	4.74668	91.934
11	5.08383	4.67374	91.933
12	5.13372	4.71946	91.931
13	5.16148	4.74490	91.929
14	5.19919	4.77992	91.936
15	5.37436	4.94088	91.934
Average...	....	....	91.933

Thus 100.000 parts of colorless argentic sulphate were found to yield 91.933 parts of argentic chloride, with a vanishingly small "probable error." If the weight of the darkened samples are used in the calculation the result becomes 91.934, a value which certainly represents the maximum. To have reduced the chief uncertainty to within such narrow limits was to have solved the problem as far as it need be solved at present. The interpretation of the result alone remains.

In comparing this result with that of Stas on argentic sulphate, it may be noted that Stas found in silver sulphate 69.203 per cent of silver. Because Richards and Wells found in argentic chloride $\frac{100.000}{132.867}100 = 75.2632$ per cent, it is clear that our results indicate $0.91933 \times 75.2632 = 69.192$ per cent of silver in silver sulphate, or 0.011 less than Stas's, one is forced to the conclusion that Stas's argentic sulphate was not completely reduced by hydrogen, and that his silver obtained in this way was no purer than the silver used in his other work. The only test of complete reduction used at the time was the solution of the residual metal in nitric acid; but this test could not reveal undecomposed sulphate and might not reveal traces of sulphide.

THE ATOMIC WEIGHT OF SULPHUR.

The interpretation of the new results is very similar to that already discussed in the preceding paper on nitrogen and silver. In this case, as in that, there are two uncertain ratios; and one of these ratios, namely, that of silver to oxygen, occurs in each. In the present case, the other uncertain ratio is that of sulphur to oxygen, while in the former case the other uncertain ratio was that of nitrogen to oxygen.

In order to obtain a complete solution of the numerical relations in either of these cases, it is therefore obviously necessary to obtain another series of results, bringing in such a ratio as that of silver to sulphur, or oxygen to sulphur, or chlorine to oxygen. Such an additional ratio is not known at present with modern accuracy. Because of the fact that silver and oxygen are concerned in each of the cases, a single new result, properly chosen, will solve both problems at once; but of course many new results with different compounds, confirming one another, are greatly to be desired. As has been said in the foregoing paper, some of these are already in the process of determination at Harvard College, and it is intended to pursue the matter further at the University of Berlin as well.

For the present it is necessary to state the interpretation of the results in a conditional manner, assuming various possible ratios between oxygen and silver, and stating the corresponding values for sulphur. In the future, when the assumed relationship is replaced by knowledge of the facts, intelligent choice can be made between the alternatives.

If oxygen is taken as 16.000, the following table gives the atomic weights of sulphur corresponding to the several atomic weights of silver.

Atomic Weight of Sulphur.

If Ag = 107.930 and Cl = 35.473, S = **32.113**
If Ag = 107.890 and Cl = 35.460, S = **32.078**
If Ag = 107.880 and Cl = 35.457, S = **32.069**

The lowest value in this case, as well as in the case of nitrogen, is the one supported by the recent work on the densities of gases.

In conclusion, it is a pleasure to acknowledge the generous assistance of the Carnegie Institution of Washington, without which the present work could not have been performed.

SUMMARY.

The most important results of the research may be briefly summed up as follows:

(1) A method for the preparation of pure argentic sulphate was devised.

(2) The specific gravity of argentic sulphate (previously fused) was found to be 5.45.

(3) Indication was obtained that Stas was unable wholly to reduce silver sulphate in hydrogen.

(4) Argentic sulphate was found to be occluded by silver chloride from solutions containing an excess of sulphuric acid.

(5) It was proved that argentic sulphate can be completely converted into silver chloride by heating in a current of hydrochloric acid gas.

(6) 100.000 parts of argentic sulphate were thus found to yield 91.933 parts of argentic chloride.

(7) The atomic weight of sulphur as calculated from this ratio, if oxygen is taken as 16.000, with several assumed values for silver is:

$$Ag = 107.93 \qquad S = 32.113$$
$$Ag = 107.89 \qquad S = 32.078$$
$$Ag = 107.88 \qquad S = 32.069$$